A Geochemical investigation of ground water and soils affected by evaporation pond seepage, at the Namakwa Sands Mineral Separation Plant (MSP)

A Dissertation
Presented to
The Science Faculty

By

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In Partial Fulfillment
Of the Requirements for the Degree

Master of Science in Environmental Geochemistry

Department of Geological Sciences

University of Cape Town
January 2004

DEDICATION

To my loving Wife and Daughter Monia and Monique

Abstract

Evaporation ponds are used for treating wastewaters in arid regions worldwide. Namakwa Sands an Anglo American plc operation, mines heavy minerals along the semi arid West Coast of South Africa. An acid effluent is generated during treatment of these heavy minerals. The effluent is neutralized and disposed of into unlined evaporation ponds. Seepage from the ponds affects the surrounding environment as well as the subsurface waters.

The main objective of this study was to investigate the effects of the seepage on the groundwater resources and potential implications for contaminant migration in the subsurface environment.

Three main areas were investigated, namely the evaporation ponds, the surrounding soils and the groundwater. The effluent entering the evaporation ponds is Na_2SO_4 dominant whereas the natural environment is NaCl dominant, therefore sulphate can be used as a tracer of effluent movement.

Analyses of trace element concentration in evaporation pond samples revealed that the raw effluent entering the evaporation ponds contains high concentrations of Th (10.4 mg/L), U (475 μg/L), As (217 μg/L) and Se (52.7 μg/L). The following elements were also high in comparison with the background boreholes, Fe (2887 mg/L) and Al (1414 mg/L). The neutralization process seems to be ineffective since the pH of the effluent in these ponds is 2.4. However, the water that accumulates in an adjacent seepage pond that formed naturally down slope of the evaporation ponds has a pH of 8.3 meaning that the soil acts well as a neutralising medium.

The soil sampled around the ponds is moderately alkaline. Therefore it will act as a good buffer for the acidic seepage. The soils can also generally be classified as saline-sodic. Trace elements of concern are Th and U, they exhibit elevated levels in comparison with the background samples.

The groundwater sampled from the boreholes around the evaporation ponds can be described as neutral but highly saline. Trace elements of concern in the groundwater are Uranium (0.61 μg/L - 29.13 μg/L), Arsenic (5.90 μg/L – 87.4 μg/L), and Selenium (33.35 μg/L – 177 μg/L), they exhibit elevated levels in relation to the boreholes used as control samples.

Based on the findings in this study the effluent entering evaporation ponds does affect the surrounding environment and subsurface groundwater. The water quality is of such a nature that it cannot be used for domestic, livestock watering or for irrigation purposes.

Acknowledgements

The author would like to sincerely thank the following people for their contributions and support to this thesis:

My supervisor Dr Alakendra Roychoudhury;

Meris Smith for her assistance and advice throughout the project.

For the technical staff in the Department of Geological Sciences (UCT):

Dr Andreas Spath and Fairoza for the ICP-MS analysis;

Patrick Sieas for analysing my samples on the IC.

Torsten Halbich Environmental Manager at Namakwa Sands for initiating this project and Ninette Marx for assisting with the sampling.

For my classmate Greg Merrett for helping me sample under difficult conditions.

Mr Lotter Lackay for his assistance during this project.

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CHAPTER 1

Introduction and Literature Review

1.1 Introduction:

Namakwa Sands, an Anglo American plc operation is a heavy minerals mining and benefaction business that operates along the West Coast of South Africa. The heavy mineral resources of Namakwa Sands occur on the coastal plain along the Atlantic Ocean and the business encompasses mining, concentration, separation, producing zircon, rutile, and ilmenite ($FeTiO_3$). Titania slag and pig iron are produced from ilmenite during smelting in a plant near Saldanha Bay export harbour (*pers. comm.* Halbich, 2003).

As part of the preparation process, the mineral separation plant (MSP) produces a hot sulphuric acid leach effluent, which is pumped to evaporation ponds. The effluent is limed at the ponds (to neutralize the acid). Some of the major contaminants are listed in Table 1.1. From the data, it can be seen that the contaminants will cause serious environmental problems if not controlled properly. The low pH of the pond effluent will enhance the mobility of toxic metals. The ponds are unlined and their main function is to allow evaporation of the effluent. However, some seepage from the ponds does occur, saturating the surrounding soils with the effluent. Seepage quality varies from acidic to neutral and slightly alkaline.

Mickley et al (as cited in Ahmed, 2000) stated that evaporation ponds were used over the centuries to remove water from saline solution, because they are relatively easy to construct and require low maintenance.

These evaporation ponds are also successfully used as a method of disposal in countries with dry and warm weather, as well as high evaporation rates (Ahmed, 2000). The evaporation ponds of Namakwa Sands are situated in an arid region with an evaporation rate of 1.7 to 1.8 m/yr (Copeland et. al., 1992).

Table 1.1: Chemical Analysis of Raw Effluent

Component	Raw Effluent (mg/l)	Pond Effluent (mg/L)
K	306	254
Na	523	471
Ca	330	393
Mg	565	400
SO_4	17977	8076
Cl	445	108
Phosphate as P	4	*n.d*
Silica as Si	7.0	12.2
Conductivity (mS/cm)	30	11
pH	1.6	2.4
Total Dissolved Solids (TDS)	19200	7040
Fe	2887	1486
Mn	23	51.4
Al	1414	925
Ti	157	33.5
Th	10.4	5.8
U (μg/L)	475	382
As (μg/L)	217	60.8
Se (μg/L)	52.7	36.4

Data from Table 4.1
n.d = not detected

1.2 Study objectives:

The main objective of this study was to investigate the effects of the disposal of sulphuric acid leach effluent in unlined evaporation ponds on the groundwater resources and potential implications for contaminant migration in the subsurface environment.

Specifically this study will look at:

1) The background chemical composition of water and soils in the study area.
2) Investigate the ground water chemistry as affected by evaporation pond seepage.
3) Investigate interaction between soil and the evaporation pond effluent.

1.3 The study area:

The study area is located next to the mineral separation plant near Koekenaap near the West Coast. The evaporation ponds are situated on a slope that slopes from north to south with a typical gradient of 1:40 (Copeland et. al., 1992).

Figure 1.1 Map of South Africa

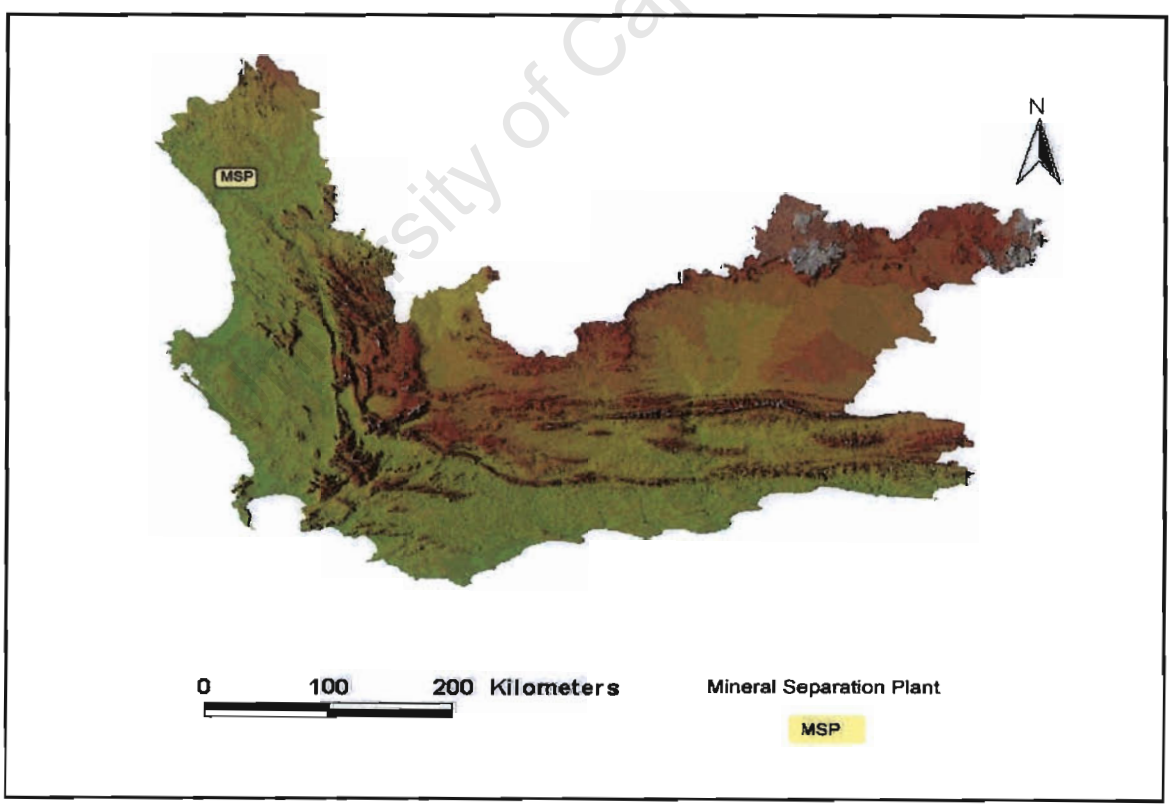

Figure 1.2 Location map of study area, indicating the Mineral Separating Plant (MSP)

1.4 Climate

The area is arid and the availability of potable water is limited to the Olifants canal system, which was built to supply fresh water to the site from the Clanwilliam dam. The site falls within the winter rainfall region, and has a rainfall of 100-200 mm per annum. Mean average temperatures are 25 to 40° C in summer, and 5 to 20° C in winter (Copeland et. al., 1992).

1.5 Geology and soils

The area is described by Toens et. al (1994) as an area that is largely underlain by granites and gneisses of the Little Namaqualand and Vioolsdrif suites. The groundwater occurs mainly in secondary aquifers (Toens et al., 1994).

The general soil profile is described by Copeland et. al (1992) as follows:
0.0 – 0.2 m Dry, orange brown, loose intact silty sand with roots. Aeolian, Topsoil.
0.2 – 1.7 m Dry orange brown, very dense to very soft rock, fissured DORBANK, pedogenic.
1.7 – 3.0 m Brown medium dense intact silty slightly calcareous SAND transported.

Bush (2001) describes the geology of the study area as follows: (4 – 12 m) upper strata of permeable sand and silt with alternating layers of less permeable iron rich dorbank and clay rich sediments. Below this is phyllitic schist with talc extending to a minimum depth of 57 m (Bush, 2001).

1.6 The Influence of Evaporation pond seepage on the groundwater and soil system: A Literature Review

1.6.1 Introduction

The evaporation method is often used for treating wastewater in arid regions (Ahmed et al. 2000). The amount of water that can be evaporated depends on the water temperature, the surface area, the specific humidity of the air mass above the water body and the air pressure (Salzman et. al., 2000). Therefore, evaporation will be enhanced during hot, dry windy periods such as found in arid areas. Salzman further states that potential advantages and disadvantages exist in treating discharged wastewater by evaporation. The advantages are that the sun provides almost all the energy required for evaporation. The process will also be further enhanced by wind. However, if the ponds are not impermeable, seepage of the wastewater may have negative impacts on the groundwater and surrounding environments (Salzman et. al., 2000).

Some of the points mentioned above are of particular concern to Namakwa Sands, because the area in which the evaporation ponds are located is situated next to a public road. It also poses an environmental risk to the groundwater that can be used by the neighboring farmers. These saline waters will also affect the soils.

1.6.2 Groundwater contaminants and their impacts

It is common knowledge that human activities are introducing contaminants into groundwater systems on an enormous scale. Examples include leaching from municipal landfills, hazardous waste burial sites, various spills, both deliberate and accidental and mine tailings. Agriculture itself causes contamination of groundwater by fertilizers and pesticides (Drever, 1997). The impact of chemical contamination in groundwater on human health or the surrounding environment depends upon many site specific criteria for example, the hydrogeology of the site, the groundwater use patterns, the degree of human exposure (Wentz, 1989). Contaminants like Th, U, As and Se listed in Table 1.1 might be a reason for concern.

1.6.3 Identification of groundwater contamination

1.6.3.1 Salinity

The salinity is a measure of the inorganic salts dissolved in water and is commonly measured as mg/l total dissolved solids (TDS), which is directly proportional to the electrical conductivity (EC) of the water (DWAF, 1996). The TDS of natural waters also varies depending on the different geological formations with which the water is in contact (DWAF, 1996).

1.6.3.2 Controls on chemical behaviour in contaminant plumes.

Redox reactions play an important role in the control and the distribution of species like O_2, NO_3^-, Fe, Mn, SO_4^{2-}, H_2S and CH_4 in groundwater systems, their redox potential will influence the fate and transport of many metals and the degradation of organic contaminants (Appelo and Postma, 1996).

According to Christensen et al. (2000) the redox conditions in groundwater can give you an indication of a pollution plume; it is also often used as a prerequisite for understanding the behaviour of the pollutants in the plume. Jensen et al. (1998) in his study stated that the organic and colloidal matter leaching from a landfill might enhance the mobility of heavy metals in leachate-polluted groundwater.

1.6.4 Contamination of soils

According to McBride (1994) EC values greater than 4 mS/cm are indicative of saline soils.

1.6.4.1 Sodicity

Soils exposed to contaminant solutions with high concentration of Na can become sodic. Useful calculations of sodicity are the exchangeable sodium percentage (ESP) and the sodium adsorption ratio (SAR). High sodium content soils swell easily and are more prone to surface crusting and erosion. The reason for this is the very high Na concentration promoting flocculation and clogging pores (Sparks, 1995). The ESP magnitude reflects the percentage of sodium on the exchange sites of the soil. SAR can be empirically related to the exchangeable sodium percentage (ESP), the percentage of exchange sites occupied by Na^+ ions by the following equation (McBride, 1994):

$$ESP/100\text{-}ESP = 0.015SAR$$

The SAR of effluent water can be used to estimate the expected ESP of the soil. Generally, ESP values greater than 15 are considered potentially toxic to plants (Evangelou, 1998).

2. Conclusion

The literature shows that contamination throughout the environment is characteristic of our advanced technological society. Industrial production often generates by-products that are of little or no economic value but that, as residual waste material, may have severe effects on the environment. The primary pathway for migration of these contaminants is the water cycle. Therefore, groundwater contamination, especially from hazardous wastes, has become a major problem. Lined evaporation ponds are recommended by Al Yaqout, (2003) as an alternative in order to protect the environment. It is also a cost-effective way to dispose of waste effluents (Al Yaqout, 2003).

CHAPTER 2

Sampling

2.1 Sampling

2.1.1 Water sampling

2.1.1.1 Introduction

According to Weaver (1992), groundwater sampling requires specialised precautions to ensure that the water sampled is representative of the *in situ* quality of groundwater in the aquifer. He also states that the following considerations need to be taken into account during groundwater sampling: Access to boreholes or well points must be available, unless the water table is shallow and the ground soft enough for augering. These need to be intelligently sited and have information on screen positions, water strikes, etc. so that you know what is being sampled. A borehole must first be purged until the field chemistry parameters (pH, EC and Eh) are stable to remove stagnant water from the borehole so that the groundwater sample subsequently collected is representative of the *in situ* groundwater. Stagnation modifies groundwater chemistry to the extent that samples may be totally unrepresentative of the formation water. For most cases, this involves the removal of three times the volume of the stagnant water in the borehole. The redox potential, alkalinity, gas composition and temperature conditions in the subsurface may be vastly different from those at the surface. For this reason it is generally recommended that measurements of pH, Eh, dissolved oxygen, temperature and even alkalinity be completed in the field immediately after bringing sample to the surface (Weaver, 1992).

2.1.1.2 Preservation and Storage of Water Samples

The chemical and physical composition of a water sample can change between sampling and analysis, due to certain reactions it might undergo (Sliwka-Kaszynska et al., 2003). The samples should be preserved and properly stored before laboratory analysis. To keep changes occurring in the sample it should be analysed as soon as possible if not, it should be protected against the changes by using appropriate preservation methods (Sliwka-Kaszynska, 2003). The appropriate containers and the correct preservation technique used all play an important role.

2.1.1.3 Evaporation pond samples

The water samples were collected in polyethylene bottles that were rinsed with MilliQ water before sampling. Four water samples were collected tabulated in Table 2.1. The sampling points are indicated in Figure 2.1. The sediment samples in the evaporation pond were collected by filling the sampling container at the sediment-water interface. Another sediment sample to a depth of no more than 2 cm was also collected. All sample containers were sealed and packed in a cooling box with ice packs. The pore waters were collected by centrifuging the sediment samples taken in the seepage pond. One set of samples was filtered in the field with a 0.45μm filter for ICP-MS analysis and acidified only for samples with a pH higher than 2. Another set were not filtered for anion analysis. Temperature, pH and electrical conductivity measurements of the four samples were taken in the field.

Table 2.1 Pond water samples

Sample name	Sample Type	Sample abbreviation	Sampling Locations GPS	
			S °	E °
Raw Effluent	Pond Water	RE	*n.t*	*n.t*
Pond Effluent	Pond Water	PE	31.46349	18.29703
Cut off Trench	Water	COT	31.46680	18.29936
Seepage pond	Water	SP	31.46837	18.29585
SP Pore water A	Sediment pore water	SP Pore A	31.46840	18.29596
SP Pore water B	Sediment pore water	SP Pore B	31.46840	18.29596

n.t = not taken

2.1.1.4 Groundwater samples

The groundwater samples were collected by purging the boreholes with a submersible pump. All the boreholes were purged, except for G4, G5 and G12 were sampled with a bailer. pH, electrical conductivity (EC) and temperature were monitored during the pumping process. The samples were collected after equilibrium of the above parameters was reached. Duplicate groundwater samples were collected in polyethylene bottles that were rinsed with MilliQ water before sampling. Nine boreholes were sampled tabulated in Table 2.2. The boreholes sampled are located around the evaporation ponds and outlined in Figure 2.1. Boreholes G9, G10, and G11 were used as control samples, because of their location related to the evaporation ponds and in order to determine the background contamination level. One set of samples was filtered in the field with a 0.45μm for ICP-MS analysis and acidified with ultrapure HNO_3. Another set were not filtered for anion analysis. Temperature, pH, Eh and Electrical conductivity measurements were taken in the field for all the samples. The samples for alkalinity measurement were added to the reagents in polyethylene vials in the field. All the samples were sealed and stored in a cooler box with ice packs.

Table 2.2 Groundwater samples

Sample name and abbreviation	Sample Type	Sampling Locations GPS	
		S °	E °
G 1	Groundwater	31.46542	18.28871
G 4	Groundwater	31.46906	18.29248
G 5	Groundwater	31.46928	18.2991
G 7	Groundwater	31.46278	18.29685
G 8	Groundwater	31.46207	18.29156
G 9	Groundwater	31.45997	18.28403
G 10	Groundwater	31.45895	18.28166
G 11	Groundwater	31.45808	18.27911
G 12	Groundwater	31.46662	18.30020

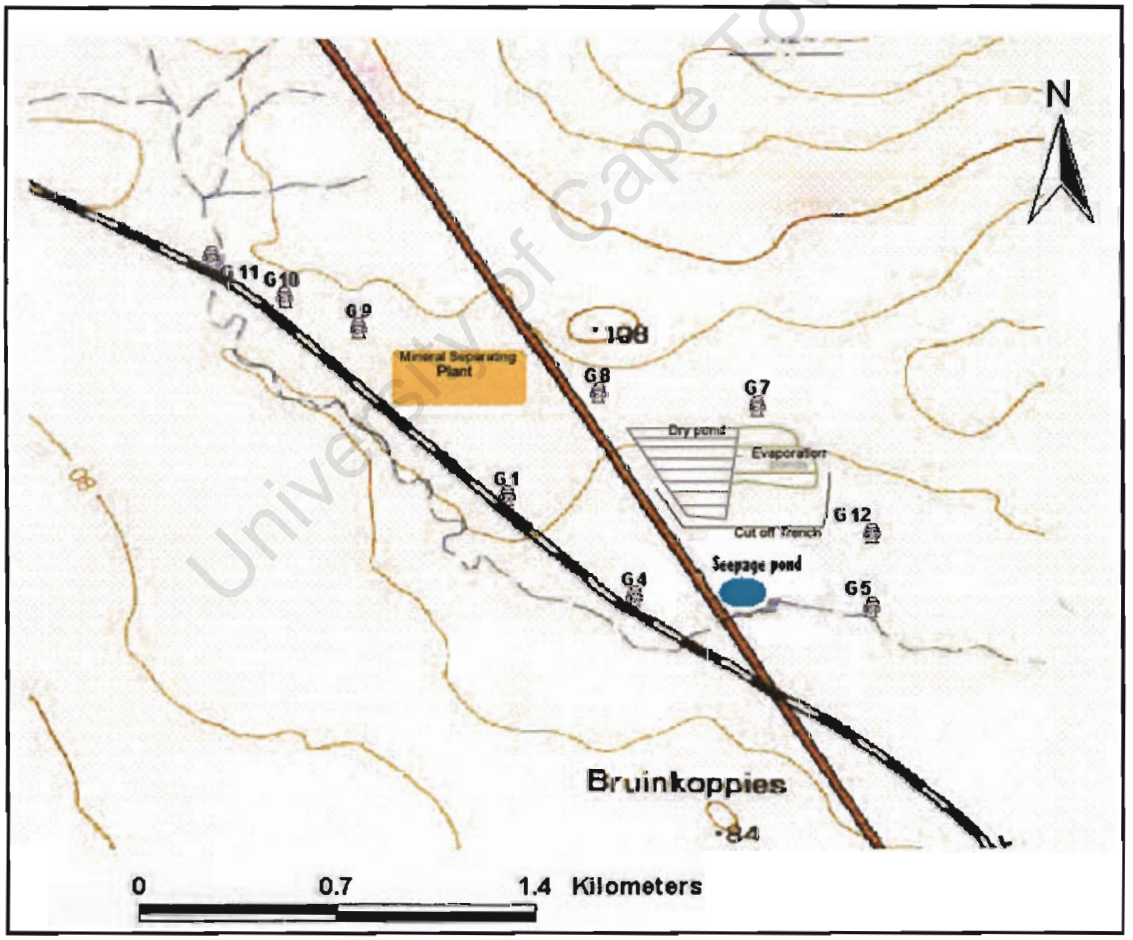

Figure 2.1 Locations of Boreholes

2.1.2 Soil/Sediment samples

The soil samples were collected predominantly on the southern side of the evaporation ponds as outlined in Figure 2.2. The reason for sampling in this area is because of the seepage that occurs here. Control samples A-C were collected on the up-hill side of the evaporation ponds at different depths in order to determine the background contamination levels. Overall 21 soil samples were collected from the topsoil as well as pits tabulated in Table 2.3. Soil samples of approximately 1 kg were collected with a spade and placed in polyethylene bags and properly sealed.

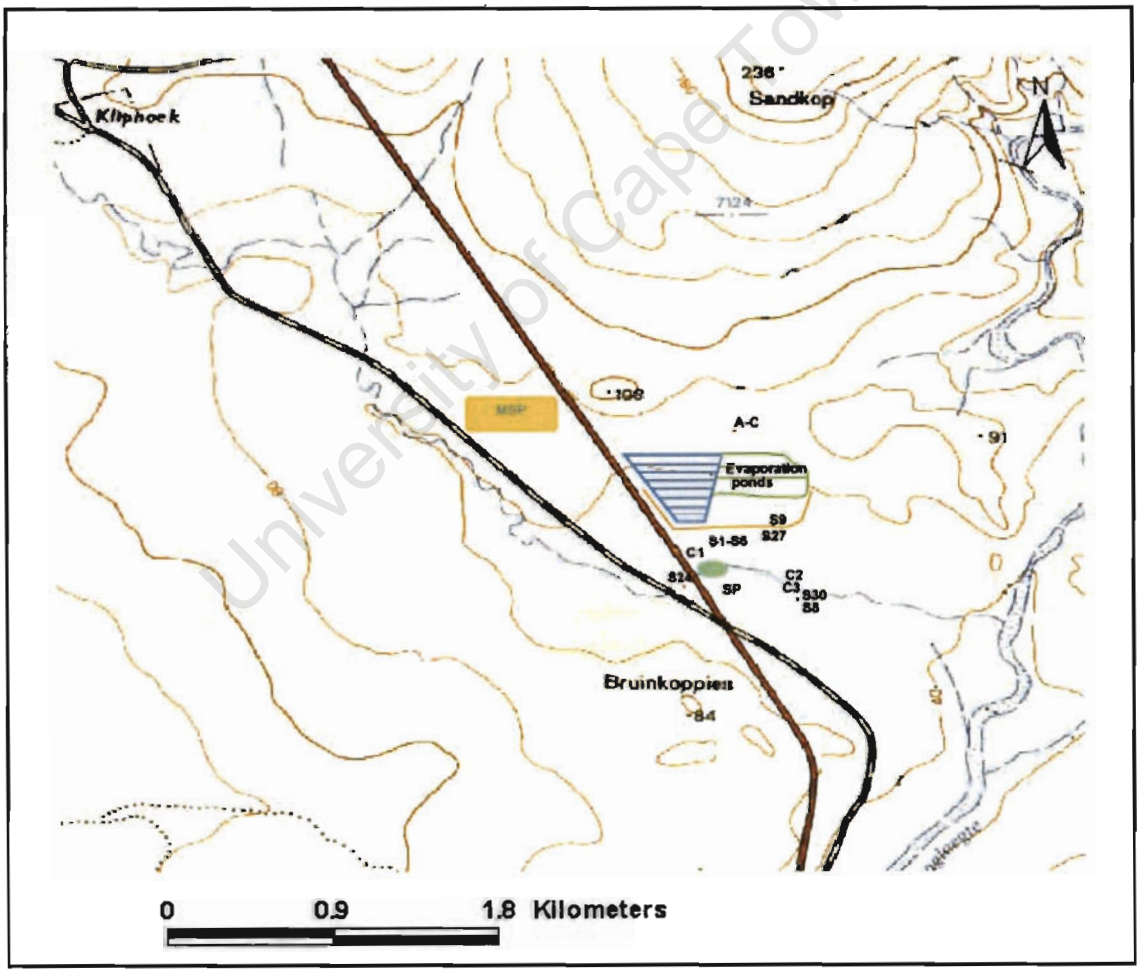

Figure 2.2 Soil sampling locations

Table 2.3. Soil/sediment samples

Sample name and abbreviation	Sample Type	Sampling Locations GPS	
		S °	E °
A	Background soil	31.46206	18.29764
B	Background soil	31.46206	18.29764
C	Background soil	31.46206	18.29764
S1	Topsoil	31.46814	18.29622
S2	Topsoil	31.46790	18.29647
S3	Topsoil	31.46773	18.29697
S4	Topsoil	31.46759	18.29720
S5	Topsoil	31.46731	18.29761
S6	Topsoil	31.46716	18.29782
Pore A	Sediment	31.46840	18.29596
Pore B	Sediment	31.46840	18.29596
S8	Topsoil	31.46986	18.30032
S9	Topsoil	31.46680	18.29936
C1	Topsoil	31.46840	18.29596
C2	Topsoil	31.46921	18.29988
C3	Topsoil	31.46950	18.29998
S24	Surface	31.46983	18.29510
S25	Pit dug (70 cm)	31.46983	18.29510
S26	Pit dug (140 cm)	31.46983	18.29510
S27	Surface	31.46734	18.29908
S28	Pit dug (25 cm)	31.46734	18.29908
S29	Pit dug (50 cm)	31.46734	18.29908
S30	Pit dug (30 cm)	31.46977	18.30023

2.1.3 Precipitate samples

Precipitate samples were also collected, one from an old dry evaporation pond sample S21 (Figure 2.3). The reason for collecting this sample is to get an indication whether the contaminant was retained in the precipitate. Another gypsum precipitate sample (S22) was also collected. A white precipitate forming on the surface of the soil near the seepage pond were also collected, sample S23 (Figure 2.4). The samples were collected in polyethylene bags and sealed.

Figure 2.3 Gypsum precipitate in old dry pond

Figure 2.4 Precipitate forming on soil surface

CHAPTER 3

Methods

3.1 Analytical methods

Most of the analyses were conducted at the University of Cape Town in the Department of Geological Sciences. Analyses were done on the following samples: ground and surface water, soil, sediment and precipitates.

3.1.1 Soil analysis

Samples were air-dried, sieved through a 2mm sieve, and stored at room temperature in the soil laboratory at the University of Cape Town. The analyses that were done on the bulk sample were: extractable acidity, Ca and Mg; pH, percentage of organic matter, particle size analysis, bulk elemental composition, and mineralogical composition. The soil solution was also analysed for pH, electrical Conductivity (EC), major cations and anions, and trace elements.

3.1.1.1 Saturated soil extract

250 g of air-dried soil sample was moistened with MQ water while stirring with a spatula to reach saturation. The pastes were allowed to equilibrate overnight, the saturated paste extract (SPE) was then obtained using a vacuum pump and filtered through a 0.45μm filter. The SPE was analysed by same methods as water samples.

3.1.1.2 pH

Three pH measurements were made using a pH meter and electrode. The pH of the samples was measured for the sample in 1:2.5 soil/solution ratio. A 10 g sample was weighed and mixed with 25 ml MilliQ water and allowed to equilibrate. The pH of the supernatant was then determined after 30 minutes. The procedure was repeated using a 1M KCl solution instead of MilliQ water.

3.1.1.3 KCl extractable acidity, Ca and Mg

For extractable acidity, a 2.5 g sieved soil sample was mixed with 25 ml of 1M KCl solution and shaken for 4 minutes. 10 ml of the supernatant was titrated with a 0.001 M standard NaOH solution using phenolphthalein indicator. A blank determination on the KCl solution was also done. The following calculation was used to calculate acidity in $mmol_c/kg$ of soil:

$$Concentration_{NaOH} \times (Volume_{NaOH} - Volume_{Blank}) = Concentration_{soil\ acidity} \times Volume_{Aliqout}$$

The remaining solution was filtered and sent to the Chemical Engineering Department at UCT for exchangeable Ca and Mg determination by Flame atomic absorption spectrometry (FAAS).

3.1.1.4 Electrical Conductivity

The electrical conductivity was measured directly in the extract, using a conductivity meter and conductivity cell and temperature probe. The EC was reported as mS/cm.

3.1.1.5 Percentage organic carbon

Organic carbon was determined using the Walkley-Black method. This method entails the oxidation of organic matter by a mixture of potassium dichromate $K_2Cr_2O_7$ and sulphuric acid.10ml of 0.167 M $K_2Cr_2O_7$ and concentrated sulphuric acid was used to oxidise the organic carbon in approximately 1.0 g of soil sample. The remaining $K_2Cr_2O_7$ was titrated with a standard $Fe(NH_4)_2(SO_4)_2$ solution. The concentration of the $Fe(NH_4)_2(SO_4)_2$ solution was determined by titrating a blank of 10 ml of 0.167 M $K_2Cr_2O_7$ solution. The calculation is as follows:

$$\text{Molar concentration of } Fe(NH_4)_2(SO_4)_2 = \frac{10 \text{ ml } K_2Cr_2O_7 \times 0.167 \text{ M} \times 6}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

The organic carbon % was determined by titrating a mixture of sample and $K_2Cr_2O_7$ solution mixture with the standardised $Fe(NH_4)_2(SO_4)_2$ solution. The calculation is as follows:

$$\text{Organic carbon \%} = \frac{[\text{ml } Fe(NH_4)_2(SO_4)_2 \text{ blank} - Fe(NH_4)_2(SO_4)_2 \text{ sample}] \times M \times 0.3 \times f}{\text{Soil mass}}$$

Where M = concentration $Fe(NH_4)_2(SO_4)_2$ and f = a recovery factor of 1.3

3.1.1.7 Major anions in soil solution: Ion Chromatography

Ion chromatography refers to modern and efficient methods of separating and determining ions based upon ion-exchange resins (Skoog, 1982). An eluent is passed through a solid stationary phase. A high-pressure pump is required to force the eluent through the column. A conductivity detector then detects the separated ions of interest. Major anions in the saturated paste extract namely, F^-, Cl^-, NO_3^-, PO_4^{-3} and SO_4^{-2} were analysed using a Dionex, DX300 series suppressed ion chromatograph. The samples were diluted such that their electrical conductivities were below 150 μS/cm.

3.1.1.8 Major cations in solution: Atomic Absorption

Atomic Absorption as already described above was used to determine the major cations namely, Na^+, K^+, Ca^{2+} and Mg^{2+}.

3.1.1.9 Trace elements in soil solution: ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) is a fast, precise, and accurate multi-element analytical technique for the determination of trace element abundances (< 0.1 wt. %) and isotopic ratios in liquid and solid samples. In ICP-MS, elemental abundances or isotopic ratios are determined by the mass spectrometry (MS) of ions generated in an inductively coupled Ar plasma (ICP). Using a stream of Ar carrier gas, liquid or solid sample material is introduced into an inductively couples Ar plasma which serves as an efficient source of positively charged analyte ions. Quantitative analysis of trace elements in the soil solution was done using an Elan 6000 inductively coupled plasma mass spectrometer (ICP-MS). The samples were diluted and an internal standard was added. The internal standard function is in the calibration of the instrument and to correct for drift. Certified NIST standards and blank samples were also analysed to assess accuracy.

3.1.1.10 Sodium Adsorption Ratio (SAR)

The SAR was determined by obtaining soil solution from the soil after saturating it with water, removing the solution by vacuum, and analyzing it for Na, Ca and magnesium (Mg) in milligrams per liter. The following formula was then used to estimate the SAR: (Evangelou, 1998). $SAR = (Na/23)/(Ca/40 + Mg/24)^{1/2}$

Where 23, 40, and 24 are the atomic weights of Na^+, Ca^{2+}, and Mg^{2+}, respectively.

3.1.1.11 Mineralogical composition of the bulk sample- X ray diffraction (XRD)

The bulk sample was ground to a fine powder and then pressed into a sample holder and was ready for analysis. The samples were analysed using a Philips PW 1390 XRD. The samples were irradiated by means of monochromatic X-rays emitted by a copper K-α X-ray tube [λ (K_α) = 1.542 Å]. The X-Ray generator was operated at 40 kV and 25 mA. The samples were scanned between 5° and 70° with a step time of 0.5 s, the scan was about 10 minutes long.

3.1.1.11 Bulk Soil analysis

50 mg of sample was weighed out accurately on the microbalance into small Savillex beakers. To each sample 4 ml of ultrapure HNO_3 was added. The beakers were closed tightly with lids and placed on hotplates for 48 hours to digest at a temperature of 50 – 60 °C. The beakers were taken off the hotplates and allowed to cool and the lids removed. The open beakers were placed on the hotplates again and left to evaporate to complete dryness. Once the samples were dried down, 2 ml of ultrapure HNO_3 was added to each sample, the beakers were then placed back on the hotplates and allowed to evaporate to complete dryness at a temperature of 75 °C. The beakers were then taken off the hotplates and allowed to cool, 4 ml of internal standard was added, and they were placed into an ultrasonic bath for 20 minutes. The samples were then quantitatively transferred into 50 ml vials, filled to 50 ml with 5% HNO_3 and weighed accurately. The samples were diluted further with 5% HNO_3 and were then analysed on the ICP-MS as described above.

3.1.1.12 Particle size analysis

The < 2.0 mm soil samples were sent to a commercial laboratory, Bemlab, for grain size analysis. The analyses were done using a hydrometer and sieves.

3.1.1.13 Phosphate sorption

A phosphate sorption isotherm was determined using Rowell's method (1994, p 209). Potassium dihydrogen phosphate was dried for an hour at 105 °C, a 100 μg P/ ml stock solution was prepared from it. A calibration curve was constructed by making known phosphate standards of 0, 0.5, 1.0, 2.0, 3.0 and 5.0 μg P/ml with 25 ml 0.4 M $CaCl_2$ and MQ water. The P contents of the samples could then be calculated from the standard calibration curve using the equation:

$$\mu g\ P/ml = [(absorbance - 0.0025) / 0.0249]$$

The samples and standards were used for colour development according to the phosphomolybdate method (5 ml sample, 8 ml ascorbic acid and 8 ml ammonium molybdate) (Rowell, 1994). The absorbance of the standards and samples were measured using a 1cm cuvette on a LKB Novaspec 4049 spectrophotometer at 880 nm. 2.5 g of each sample was placed into seven 50 ml vials with 25 ml of each phosphate standard and was placed on a shaker for 24 hours. The samples were placed in a centrifuge for 5 minutes and 5ml of the supernatant was used for colour development.

The final concentration was calculated from the calibration curve and subtracted from the original individual phosphate concentrations, multiplied by 25 ml and divided by 2.5 g of soil, to give concentration P adsorbed.

3.1.2 Water analysis

Water samples were taken from nine boreholes, two evaporation ponds, the raw effluent entering the evaporation ponds, a cut off trench as well as pore water from two sediment samples. The samples were taken in duplicate for all the analyses. One set of samples was filtered and acidified for ICP-MS analysis and another set was unfiltered and unacidified for the other analysis. All water samples were kept below 4° C before analysis.

3.1.2.1 pH

pH measurements were taken in the field using a pH meter and electrode. The pH meter was calibrated by using pH 4.0 and pH 7.0 buffer solutions.

3.1.2.2 Electrical Conductivity

The electrical conductivity was measured using a conductivity meter and conductivity cell and temperature probe. The meter and probe were calibrated by using a 0.01 M KCl solution. Measurements were made in the field as well as in the laboratory; the EC was reported as mS/cm.

3.1.2.3 Eh determination

Eh measurements were taken in the field with a pH meter and Eh electrode (platinum combined with silver: silver chloride reference). The Eh values were calculated by adjusting the difference in potential between the hydrogen electrode and the chosen reference electrode.

The half-cell potential is also dependent on the type of electrode, filling solution concentration and temperature. Eh reference solutions provide stable known Eh values over a range of temperatures. A Zobell reference solution was used in the measurements for Eh.

3.1.2.4 Alkalinity

Alkalinity is primarily controlled by carbonate species and is therefore usually expressed in terms of equivalence to calcium carbonate ($CaCO_3$). Briefly, carbon dioxide dissolves in water to form carbonic acid (H_2CO_3), which, depending on pH, dissociates to form, carbonate, bicarbonate and hydrogen ions (DWAF, 1996).

Alkalinity was measured using a spectrophotometric method. The method was proposed by Sarazin et al. (1999) to determine the alkalinity in seawater. All the basic species taken into account in the alkalinity expression are neutralised by a weak acid (formic acid) mixed with a pH sensitive dye, bromo-phenol blue, which has a dissociation constant close to those of formic acid (Sarazin et. al 1999). The following reagents were prepared: Colored reagent (CR) 25 ml of 0.1 M methanoic acid (formic acid) and 25 ml bromophenol-blue (500 mg L^{-1}) in 250 ml, diluted with 0.7 NaCl solution. Standards and samples were prepared by mixing 2 ml of CR with 2ml of standard or sample in polypropylene vials. The absorbances of the standards and samples were then measured at 590 nm on a spectrophotometer. A calibration curve was constructed from standard $NaHCO_3$ solutions at concentrations of 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0 mM. By fitting a second order polynomial function to the curve, the unknown concentrations of the samples were then determined using the equation:

$$mM\ NaHCO_3 = [-1.7659\ (absorbance)^2 + 9.4359\ (absorbance) - 2.1465$$

3.1.2.5 Major anions in water samples: Ion Chromatography

Major anions in the water samples namely, F^-, Cl^-, NO_3^-, PO_4^{-3} and SO_4^{-2} were analysed using a Dionex, DX300 series suppressed ion chromatograph. Prior to analysis the samples were filtered through a 0.45 μm filter in the field. The samples were diluted such that their electrical conductivities were below 150 μS/cm.

3.1.2.6 Major cations in solution: Atomic Absorption

Atomic Absorption as already described was used to determine the major cations namely, Na^+, K^+, Ca^{2+} and Mg^{2+}.

3.1.2.7 Phosphorous

Phosphorous occurs in natural waters and in wastewaters almost solely as phosphates (Eaton, 1995). Phosphate is determined by using Standard Method 4500-P E (Eaton, 1995), the ascorbic acid method. 50 ml of samples were added to 8 ml of a combined reagent (ammonium molybdate, antimonyl tartrate and ascorbic acid). After at least ten minutes but not more than thirty, the absorbance readings were taken at 880 nm on a spectrophotometer. A set of standards ranging from 0.25 and 1.00 mg/L as well as a blank were measured and a calibration curve was constructed to determine the concentrations of the samples using the following equation:

$$\text{mg P/L} = [(\text{absorbance} - 0.007) / 0.6966]$$

3.1.2.8 Silica by Colorimetry

Degradation of silica-containing rocks results in the presence of silica in natural waters as suspended particles, in a colloidal or polymeric state, and as silicic acids or silicate ions (Eaton et al., 1995). Silica was determined colorimetrically by Standards Methods 4500-Si D, the molybdosilicate method. 50 ml of unfiltered samples and standards were mixed with 1ml HCl, 2ml ammonium molybdate reagent and 2 ml oxalic acid. The absorbances were then taken after 5 minutes after adding the oxalic acid. Measurements were made at 410 nm using a LKB Novaspec 4049 spectrophotometer. Oxalic acid is added to destroy the molobdophosphoric acid but not the molybdosilicic acid. The intensity of the yellow colour is proportional to the concentration of "molybdate reactive " silica (Eaton et al., 1995). A set of standards ranging from 1.0 to 20.0 mg/L as well as a blank were measured and a calibration curve was constructed to determine the concentrations of the samples using the following equation:

$$\text{mg } SiO_2/L = [(\text{absorbance} - 0.0531) / 0.0.0519]$$

3.1.2.9 Fluoride

Fluoride was determined using a Metrohm 692 pH Ion Meter and fluoride ion selective electrode. The electrode was calibrated by using 6 standards. In order for the samples and standards to be of the same ionic strength, an ionic strength adjustment buffer was added (TISAB) to both the samples and standards. The standards were diluted with TISAB solution 1:1 and measured on the mV range of the pH Ion Meter under continuous stirring, beginning with the most dilute solution. The measured values were stored in the pH Ion meter and a calibration curve is constructed. The samples were also diluted with TISAB solution 1:1 and measured as described above.

3.1.2.10 Elemental Analysis: ICP-MS

The same procedures were followed for the analysis of the water samples as for the soil solutions.

3.1.3 Analytical appraisal

3.1.3.1 Charge balance

According to the principle of electro neutrality, all solutions are electrically neutral; that is, there is no solution containing a detectable excess of positive or negative charge, because the sum of the positive charges equals the sum of negative charges (Christian, 1994). If the charges do not balance, there is an indication of erroneous analysis. The charge balances for all solutions were calculated using the PHREEQC modeling programme.

3.1.3.2 PHREEQC model

PHREEQC is a computer program written in the C programming language that is designed to perform a variety of aqueous geochemical calculations. PHREEQC is based on an ion-association aqueous model and has capabilities for (Parkhurst and Appelo, 1999):

i). Speciation and saturation-index calculations; ii). reaction-path and advective-transport calculations involving specified irreversible reactions, mixing of solutions, mineral and gas equilibria, surface-complexation reactions, and ion-exchange reactions; iii) and inverse modeling, which finds sets of mineral and gas mole transfers that account for composition differences between waters, within specified compositional uncertainties.

CHAPTER 4

Results

4.1 Analysis of raw effluent, evaporation ponds, and cut-off trench.

4.1.1 Water analysis

The results of analyses of water samples from the raw effluent, evaporation ponds and cut off trench are tabulated in Table 4.1.The waters are characterized by very high salinity that ranges from 11.21 mS/cm to 29.7 mS/cm with low pH except for the seepage pond with a pH of 8.33. For most natural waters, EC is related to the total dissolved solids (TDS) concentration by a conversion factor (McBride, 1994):

EC (mS/cm at 25° C) x 640 = mg/L TDS

The raw effluent water is characterized by a dominance of SO_4^{2-}. The total elemental analysis done by ICP-MS indicates elevated concentrations of various metals, especially for the raw effluent. Al, Ti, Fe, levels are much higher than the other samples. Si concentration increases in the cut off trench sample.

Table 4.1 Surface water samples: General Results

	Raw Effluent	Pond Effluent	Cut off trench	Seepage pond (SP)	SP Pore Water A	SP Pore Water B
°C	29.2	20.4	17.9	15.3	*n.a*	*n.a*
Alkalinity, mg $CaCO_3$/L	*n.a*	*n.a*	*n.a*	417	*n.a*	*n.a*
pH	1.6	2.4	4.1	8.3	*n.a*	*n.a*
EC (Field) mS/cm	30	11	14	30	*n.a*	*n.a*
EC (Lab) mS/cm	34	12	14	30	*n.a*	*n.a*
TDS, mg/L	19200	7040	8960	19200	*n.a*	*n.a*
Anions (mg/L)						
Cl^-	445	108	728	6679	9597	8852
F^-	22	24	17	*n.d*	*n.d*	*n.d*
Br^-	82	*n.d*	*n.d*	*n.d*	*n.d*	*n.d*
NO_2	*n.d*	*n.d*	25	*n.d*	*n.d*	*n.d*
PO_4	4	*n.d*	*n.d*	*n.d*	*n.d*	*n.d*
SO_4^{-2}	17977	8076	7761	8086	14972	11309
NO_3	*n.d*	78	*n.d*	*n.d*	*n.d*	*n.d*
Cations (mg/L)						
Na^+	523	471	1427	5790	1168	8330
Ca^{2+}	330	393	399	661	378	440
K^+	306	254	245	146	265	201
Mg^{2+}	565	400	980	770	1275	845
Elemental Concentrations (mg/L)						
B	1.1	1.0	9.9	8.8	14.5	8.4
Al	1414	925	462.6	0.003	0.1	0.3
Si	7.0	12.2	36.1	4.6	23.8	19.1
Ti	156.5	33.5	1.6	1.6	2.4	1.9
V	13.7	6.7	0.02	0.1	0.1	0.1
Cr	35.9	20.9	2.1	0.004	0.03	0.01
Mn	22.62	51.4	67.4	0.4	1.1	12.3
Fe	2887	1486	1.9	0.6	1.0	0.7
Ni	1.75	1.2	1.5	0.02	0.02	0.03
Zn	7.24	2.4	0.4	0.3	0.5	0.4
Rb	1.68	1.4	0.1	0.003	0.1	0.04
Sr	5.67	2.6	7.0	6.9	7.5	8.8
Zr	20.2	1.5	0.002	0.002	0.01	0.01
Pb	1.2	0.2	0.002	0.001	0.01	0.01
Th	10.4	5.8	0.1	*n.d*	*n.d*	*n.d*

n.d = not detected n.a = not analysed

Table 4.1 Surface water samples: General Results (cont.)

	Raw Effluent	Pond Effluent	Cut-off trench	Seepage pond (SP)	SP Pore Water A	SP Pore Water B
Elemental Conc. (µg/L)						
U	475	382	605	31.4	25.7	96.0
Li	504	423	697	44.9	75.8	48.3
Be	44.2	31.5	115	*n.d*	2.6	3.1
Co	392	300	106	2.8	3.3	13.1
Cu	474	301	30.6	44.4	96.0	77.4
As	217	60.8	16.9	49.9	154	59.6
Se	52.7	36.4	46.4	88.1	156	133
Mo	23.3	7.69	2.4	4.9	4.0	119
Ag	84.0	7.83	1.0	0.8	1.2	0.5
Cd	10.5	7.79	7.9	1.0	1.2	0.5
Hg	6.86	2.48	1.4	1.0	1.3	0.9
Ba	447	444	33.6	26.5	56.1	84.5

n.d = not detected

4.2 Soil and sediment analysis

4.2.1 Soil description

Table 4.2 Soil description

Sample no.	Horizon	Depth (cm)	*Munsell Dry	
A	A	5	2.5 YR 6/6	Red
B	B	100	7.5 YR 5/8	Strong brown
C	C	250	5 YR 6/8	Reddish yellow
S1	A	5	5 YR 5/4	Reddish brown
S2	A	5	*n.i*	*n.i*
S3	A	5	*n.i*	*n.i*
S4	A	5	*n.i*	*n.i*
S6	A	5	*n.i*	*n.i*
C1	A	5	5 YR 5/6	Yellowish Red
C2	A	5	5 YR 6/3	Light Reddish brown
C3	A	5	5 YR 7/2	Pinkish gray
S8	A	5	5 YR 7/4	Pink
S9	A	5	5 YR 6/4	Light Reddish brown
S24	A	5	5 YR 6/4	Light Reddish brown
S25	B	70	5 YR 7/4	Pink
S26	C	140	5 YR 7/4	Pink
S27	A	5	5 YR 5/6	Yellowish red
S28	B	25	5 YR 5/6	Yellowish red
S29	C	50	5 YR 5/6	Yellowish red
S30	A	30	5 YR 7/3	Pink

* Munsell color codes (HueValue/Chroma) and descriptions (Munsell color, 1992). n.i = not identified

4.2.2 Analytical Results for soil and sediment samples

Analyses as described in Chapter 3 were conducted and interpreted in order to gain a geochemical understanding of the soil. The analyses were done on the bulk sample and the saturated soil extract as well as the two sediment samples.

4.2.3. General Results

Table 4.3 Soil samples: General Results

Sample no.	pH			1 M KCl extractable ($mmol_c/kg$ soil)			Particle size distribution (%) < 2 mm				% Organic Carbon
	MQ	1 M KCl	Δ pH	Acidity	Ca^{2+}	Mg^{2+}	Coarse Sand	Sand fraction	Silt	Clay	
A	8.5	7.9	-0.6	0.6	25.2	24.6	9.4	72.8	7.6	10.2	0.2
B	8.0	7.1	-0.9	0.9	24.9	60.6	8.1	67.5	6.6	17.8	0.04
C	8.3	7.8	-0.5	0.1	23.6	58.5	16.9	64.3	5.2	13.6	0.0
S1	8.9	8.1	-0.8	0.9	29.2	37.0	10.3	68.7	6.0	15.0	0.1
S2	6.4	5.7	-0.7	1.0	400.7	131.8	31.4	49.6	5.8	13.2	0.3
S3	8.8	8.4	-0.4	*n.a*	33.4	27.3	7.7	71.9	7.6	12.8	0.3
S4	9.5	8.1	-1.4	*n.a*	37.9	10.2	15.6	65.2	7.6	11.6	0.03
S5	9.0	8.5	-0.5	0.3	97.8	19.6	18.4	62.6	6.8	12.2	0.1
S6	9.0	8.4	-0.6	0.3	167.7	16.1	11.5	67.5	6.2	14.8	0.1
C1	7.1	6.5	-0.6	1.6	298.6	189.5	11.2	72.6	4.4	11.8	0.2
C2	8.4	7.8	-0.6	0.6	94.8	99.1	5.8	69.4	9.4	15.4	0.5
C3	8.0	7.5	-0.5	0.1	114.9	180.7	5.0	56.2	19.6	19.2	0.8
S8	9.0	8.5	-0.5	0.1	157.2	37.4	21.1	59.1	8.2	11.6	0.1
S9	4.8	4.2	-0.6	29.5	169.7	27.2	16.3	60.5	7.8	15.4	0.9
S24	7.5	7.1	-0.4	*n.a*	41.2	26.6	19.0	63.6	7.6	9.8	0.3
S25	7.6	6.5	-1.1	0.2	8.4	13.5	29.5	54.3	4.0	12.2	0.01
S26	7.7	6.7	-1.0	0.1	10.6	17.5	32.6	56.0	0.6	10.8	0.002
S27	7.9	7.4	-0.5	0.4	65.0	186.8	9.5	65.5	10.0	15.0	0.7
S28	6.6	6.0	-0.6	*n.a*	12.7	88.9	13.7	53.3	3.6	29.4	0.2
S29	5.5	4.7	-0.8	1.2	20.0	82.5	20.9	56.5	3.6	19.0	0.0
S30	8.0	7.5	-0.5	*n.a*	34.2	33.8	34.7	42.3	7.8	15.2	0.2
Pore A	9.0	8.4	-0.6	0.2	94.7	131.3	8.1	50.5	15.4	26.0	1.6
Pore B	8.4	7.6	-0.8	*n.a*	19.9	31.4	14.6	66.0	6.6	12.8	0.1

n.a = not analysed

Table 4.4 Soil saturated paste Extract results

Sample no.	pH	EC mS/cm	Major anions- IC (mg/L)					Major cations – AA (mg/L)			
			Br^-	NO_3^-	Cl^-	SO_4^{2-}	PO_4^{3-}	Na^+	Mg^{2+}	Ca^{2+}	K^+
A	7.7	39.2	*n.d*	188.3	13039	1621.0	125	1289	900	1247	261
B	7.2	55.0	*n.d*	279	19948	4043	236	11110	1720	1056	374
C	7.3	54.7	*n.d*	217.5	20571	3690.0	234	2056	1935	1223	321
S1	7.9	16.8	*n.d*	33.1	736	275.5	59	513	354	480	170
S2	5.9	64.5	*n.d*	317.0	23389	4544.0	237	1589	5547	2253	176
S3	7.5	59.7	*n.d*	416.5	21375	2011.0	236	1550	1223	1726	434
S4	8.5	8.9	3.9	22.5	998	3275.1	48	219.9	55.1	360	96
S5	7.7	72.5	*n.d*	149.5	24112	4747.0	233	6269	2355	1888	310
S6	8.2	27.5	*n.d*	32.0	5951	5393.5	*n.d*	762	374	878	155
C1	5.5	166.7	*n.d*	416.3	84641	11313.8	*n.d*	1626	8896	1351	777
C2	7.3	139.7	*n.d*	525	60618	25813	*n.d*	1134	7576	859	1067
C3	7.1	165.4	*n.d*	467.5	75025	17712.5	585	6381	9258	1008	981
S8	8.2	50.9	*n.d*	120.5	11583	18257.5	256	*n.a*	*n.a*	*n.a*	*n.a*
S9	5.0	10.1	4.0	27.7	1249	4787.3	47	134.0	603	614	157
S24	7.7	23.8	*n.d*	94.8	7705	661.5	*n.d*	1196	1045	1713	200
S25	7.3	30.6	*n.d*	*n.d*	7848.3	4531.9	*n.d*	6615	572	379	178
S26	7.2	42.1	*n.d*	307.5	13680.5	6602.5	*n.d*	9407	975	671	222
S27	6.8	219	*n.d*	1483.8	124326.3	10601.3	*n.d*	85707	13789	1347	1830
S28	7.7	79.3	*n.d*	449	27303	4866	*n.d*	16279	4013	785	291
S29	5.3	67.3	*n.d*	414.5	24390.5	5306.5	*n.d*	14421	2328	673	245
S30	7.4	62.5	*n.d*	*n.d*	18881	9875	*n.d*	14520	1407	665	221
Pore A	7.9	80.7	*n.d*	240	16132	24635	*n.d*	7544	5509	838	885
Pore B	7.8	53.8	*n.d*	184	12717	17336	239	744	2738	674	559

n.d = not detected n.a = not analysed

Table 4.5 Saturated paste Extract results

	B	S 2	S 5	Pore A	S 24	S 25	S 26	S 27	S 28	S 29	S 30
Elemental Concentrations (mg/L)											
B	15.2	3.3	15.9	20.3	0.2	6.4	7.8	2.8	2.5	5.8	3.3
Si	11.4	27.4	10.2	12.3	13.1	26.7	19.8	1.3	13.4	28.4	8.2
Ti	2.1	4.9	4.5	5.9	3.0	1.2	1.7	2.7	1.7	1.3	1.7
Mn	0.4	12.2	0.03	1.1	1.8	0.2	0.3	2.2	1.4	3.1	17.6
Fe	4.0	6.7	5.1	2.8	8.5	1.6	2.8	4.9	2.7	2.1	2.4
Cu	0.1	0.2	0.3	0.3	0.02	0.05	0.1	0.8	0.2	0.2	0.1
Zn	0.2	0.3	0.3	0.7	0.05	0.2	0.3	0.5	0.2	0.2	0.3
Sr	15.8	16.9	39.8	22.2	12.4	4.6	7.8	47.2	13.4	12.1	6.9
Elemental Concentrations (µg/L)											
Li	153	55.8	172	193	40.8	42.4	96.8	784	130	168	92.1
Al	37.4	40.5	48.0	162	17.8	33.1	33.7	22.0	14.6	102.8	20.8
As	143	194	214	250	63.6	58.6	75.0	792	178	132	90.7
Se	329	260	35.8	564	111	108	199	*n.d*	343	292	156
Cd	1.43	18.1	1.1	1.58	2.0	1.0	2.4	140.9	13.6	9.07	6.35
Pb	4.5	6.05	2.83	3.04	2.1	3.0	4.7	24.4	9.82	12.2	4.5
Th	0.04	0.79	0.29	0.63	0.1	0.1	0.1	0.29	0.2	0.9	0.1
U	0.1	0.58	10.6	174	4.7	0.2	0.3	0.31	0.6	0.4	0.4
Ba	53.2	407	141	117	801	101	96.0	224	25.0	61.9	147
Cr	17.3	19.2	29.1	29.8	5.0	2.9	7.7	20.8	14.2	8.8	7.7
V	100	120	292	91.9	12.7	30.9	40.2	540	124	76.6	56.2

n.d = not detected

4.2.4 Derived parameters

Sodium adsorption ratio of the soil solution was calculated from the concentration of Na^{+}, Ca^{2+} and Mg^{2+} obtained from AA analysis listed in Table 4.4, while base saturation and effective cation exchange capacity (ECEC) were calculated from KCl extractable Ca, Mg and acidity (Table 4.3). The details of the calculation are presented in Appendix C.

Table 4.6 Derived Parameters

	B	S 2	S 5	Pore A	S 24	S 25	S 26	S 27	S 28	S 29	S 30
ECEC ($mmol_c/kg$)	86.4	533.5	117.7	226.2	-	22.1	28.2	252.2	-	103.7	-
Base saturation (%)	98.9	99.8	99.8	99.9	-	99.1	99.7	99.8	-	98.8	-
Acid saturation (%)	1.1	0.2	0.2	0.1	-	0.9	0.3	0.2	-	1.2	-
SAR $(mmol_c/L)^{-½}$	49.1	4.1	22.7	20.9	5.6	50.1	54.3	152.1	52.1	59.1	73.2
ESP (%)	71.3	10.8	48.6	39.9	23.3	81.4	78.3	75.6	65.7	73.6	80.9

4.2.5 Bulk composition

ICP-MS analysis was used to determine the bulk chemical composition of the soil and sediment solid phase. Both the major bulk elemental composition and the trace bulk elemental composition of the samples are tabulated in Table 4.7.

Table 4.7 Bulk analyses of soil and sediment samples

	B	S2	S5	Pore A
Conc.mg/kg				
Na	8077	11163	14340	22940
K	17055	23245	35177	22181
Mg	7327	5904	3755	7330
Ca	2086	17373	5174	18558
B	55.7	34.6	30.7	56.4
Al	56055	66043	61352	51903
Si	284.18	566.28	360.73	350.93
Ti	2542	3222	2195	1905
V	69.7	65.4	35.2	37.1
Mn	199	245	330	236
Fe	25722	29222	15329	19950
Sr	91.9	132	93.2	307
Th	12.5	13.8	7.29	9.39
U	2.11	2.15	1.30	3.64
Li	23.1	20.6	15.5	21.2
Zn	80.0	110	56.4	39.2
Pb	15.2	22.2	22.7	10.4
Zr	43.2	54.8	28.3	27.4
Cr	59.3	60.9	31.3	37.5
Ni	19.8	15.6	8.81	12.4
Co	6.89	6.18	5.37	6.41
Cu	38.3	25.9	14.2	14.5
As	6.53	4.74	2.22	1.87
Se	n.d	0.36	n.d	0.26
Rb	82.2	139	171	117
Ba	291	447	666	468

Table 4.8 Bulk analyses of soil and sediment samples (cont.)

Conc.mg/kg	S 21	S 22	S 23	S24	S25	S26	S27	S28	S29	S30
Na	1772	14525	172421	4723	11633	10099	24224	14307	12035	11715
K	3038	3039	10859	14561	27452	19839	23137	25048	21447	22762
Mg	5130	15266	6177	1551	1115	872	7943	4581	6313	3390
Ca	207234	237720	33846	1168	1493	1281	3472	1694	1438	2293
B	46.7	18.4	20.6	1.15	4.47	n.d	14.1	19.7	24.5	14.1
Al	41307	3305	22122	29985	45518	34733	49482	60324	71160	49754
Si	-	345.5	56993	74.68	179.59	138.12	415.73	381.29	680.54	118.60
Ti	6333	7505	1183	1609	2091	1698	2798	2307	2624	2212
V	262	48.1	19.7	26.8	28.4	23.6	45.2	49.7	72.1	44.2
Mn	3115	616	103	99.1	89.9	89.5	677	237	250	301
Fe	91993	12808	8290	12243	12791	12885	19034	22725	35526	18823
Sr	113	187	376	52.8	55.6	44.0	99.0	74.2	74.9	109
Th	386	235	6.46	5.94	9.08	5.18	11.0	11.0	15.71	8.68
U	25.7	8.62	2.59	0.77	1.47	1.39	1.46	1.59	2.30	1.32
Li	23.5	8.21	10.6	12.7	9.20	8.13	73.0	21.7	30.9	18.8
Zn	177	154	41.1	39.3	43.6	36.3	69.7	84.8	112	68.9
Pb	29.1	47.7	6.91	14.5	27.9	16.8	11.5	22.3	19.6	19.9
Zr	2073	2664	43.5	14.9	23.2	14.0	37.8	40.5	57.7	35.0
Cr	1074	57.3	15.7	21.8	26.0	20.9	40.4	46.2	69.6	37.6
Ni	92.2	14.7	5.15	5.41	4.72	4.26	12.9	12.1	18.5	11.1
Co	10.7	1.73	2.03	2.06	2.30	1.92	6.02	5.22	6.58	5.57
Cu	18.4	6.88	7.51	10.5	9.74	7.02	14.8	17.0	25.3	16.0
As	5.93	5.33	1.63	1.68	2.05	1.42	3.30	3.56	4.99	2.37
Se	4.11	2.26	1.11	0.74	n.d	n.d	n.d	0.08	1.27	0.19
Rb	5.08	15.7	51.8	78.1	145	105	123	141	136	120
Ba	56.1	74.7	197	364	550	529	502	507	369	476

4.2.6 Phosphate sorption

The van Bemmelen-Freundlich equation was used to interpret the phosphate isotherms (Appendix C): $q_i = Ac_i^{\beta}$, where q_i = amount of P adsorbed, c_i = equilibrium concentration of P in soil solution, A and β are adjustable parameters (Sposito, 1989).

Table 4.9 Phosphate Sorption Parameters

Sample no.	Van Bemmelen Freundlich		Estimated sorption capacity mg/kg
	R^2	q_i	Q_M
S1	0.964	$76c_i^{1.0}$	242.3
A	0.989	$18c_i^{0.9}$	217.3
B	0.989	$33c_i^{0.6}$	216.8
Pore B	0.994	$54c_i^{0.6}$	226.0
C1	0.999	$23c_i^{0.8}$	214.8
C2	0.977	$16c_i^{1.1}$	219.3
S24	0.976	$24c_i^{0.8}$	217.3
S26	0.989	$19c_i^{0.8}$	211.7
S27	0.983	$18c_i^{1.1}$	226.5
S28	0.976	$22c_i^{1.1}$	218.8
S29	0.919	$65c_i^{0.4}$	223.4
S30	0.991	$26c_i^{0.8}$	90.8

Table 4.10 Mineralogy of bulk samples

Sample	Mineral (d-spacing of characteristic peak in Å)
S 21	Gypsum (7.67), Gypsum (4.30), Gypsum (3.07), Gypsum (2.88)
S22	Gypsum (7.59) Gypsum (3.06), Gypsum (4.28), Gypsum (2.87)
S23	? Marabilite (5.51), Thenardite (3.84,2.78), Quartz (3.34)
A	K-feldspar (3.35,3.26), Quartz (1.82, 1.54)
B	K-feldspar (3.36,3.25), Quartz (1.82, 1.54)
C	K-feldspar (3.37), Quartz (1.82)
Pore A	K-feldspar (3.37,3.27), Quartz (1.82)
Pore B	K-feldspar (3.36,3.26), Quartz (1.82)
C1	K-feldspar (3.35,3.25), Quartz (1.82)
C2	K-feldspar (3.36,3.26), Quartz (1.82)
C3	K-feldspar (3.35,3.24), Quartz (1.82)
S1	K-feldspar (3.35,3.25), Quartz (1.82)
S5	K-feldspar (3.36,3.26), Quartz (1.82)
S24	K-feldspar (3.35,3.26), Quartz (1.82)
S27	K-feldspar (3.35,3.25), Quartz (1.82)
S30	K-feldspar (3.36,3.26), Quartz (1.82)

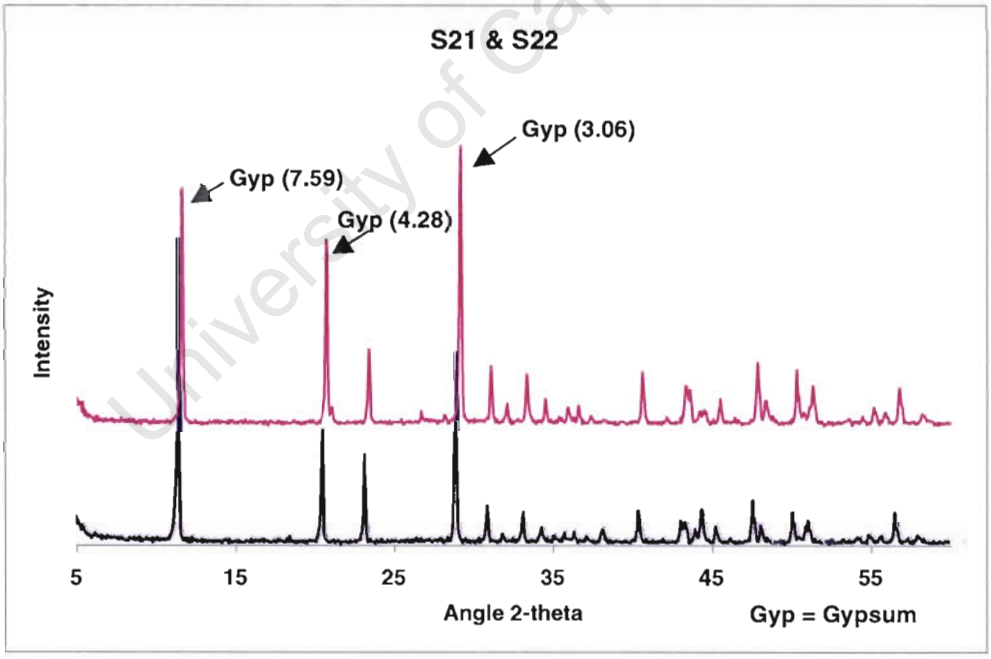

Figure 4.1 Diffractograms of gypsum precipitates

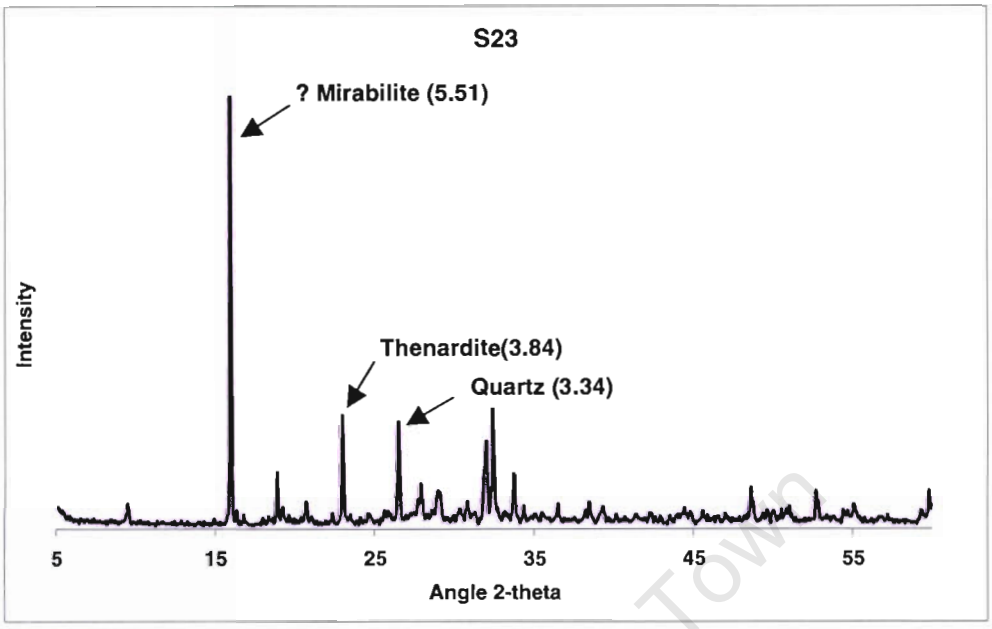

Figure 4.2 Diffractogram of soil surface precipitate

4.3 Groundwater analysis

Table 4.11 Groundwater samples: General Results

	G 1	G 4	G 5	G 7	G 8	G 9	G 10	G11	G12
°C	22.3	21.9	21.7	22.7	22.5	22.3	22.2	22.8	22.1
Alkalinity, $CaCO_3$ mg /L	231.19	251.32	258.64	189.71	198.25	217.16	183	147.62	80.52
HCO_3^- meq/L	3.79	4.12	4.24	3.11	3.25	3.56	3.00	2.42	1.32
pH (Field)	7.2	7.3	6.7	7.1	7.2	7.0	6.8	6.8	5.1
pH (Lab)	7.4	7.6	6.9	7.4	7.4	7.6	7.4	7.3	5.4
EC (Field) mS/cm	27.2	10.57	50.3	37.5	9.23	8.42	7.93	8.42	27.0
EC (Lab) mS/cm	26.9	10.41	49.45	35.0	9.06	8.32	7.78	8.37	26.65
TDS, mg/L	17408	6764.8	32192	24000	5907.2	5388.8	5075.2	5388.8	17280.0
pe	6.74	6.38	5.02	6.48	6.33	6.31	6.91	7.13	8.12
Anions (mg/L)									
Cl^-	3831	2873	12396	9570	1010	2321	2218	2337	7086
F^-	2.25	1.99	0.66	2.97	3.09	2.58	1.67	1.70	1.26
PO_4	2.8	5.6	27.6	4.4	6.0	5.0	6.6	5.8	4.0
SO_4^{2-}	1384	486	7313	2228	2308	828	422	415	2545
Cations (mg/L)									
Na^+	1965	1796	10646	6698	1237	1429	1289	1445	5327
Ca^{2+}	585	192	829	696	259	150	143	151	417
K^+	185	52	208	161	96	59	55	49	133
Mg^{2+}	625	172	1413	900	332	145	143	151	581
Charge Balance Error %	10.20	3.50	11.71	12.24	10.67	-2.61	0.75	4.29	9.45
Elemental Concentrations (mg/L)									
Si (ICP-MS)	14.46	7.42	16.51	5.24	13.94	1.14	15.00	14.99	7.04
Si (col)	22.90	11.92	21.85	9.63	22.04	17.88	23.19	22.71	12.01
Ti	1.14	0.35	1.72	1.08	0.67	0.26	0.27	0.29	0.99
Fe	1.31	0.43	2.27	1.64	0.67	0.26	0.32	0.33	1.13
Sr	4.19	1.66	8.45	5.99	1.95	0.93	1.08	1.08	4.71
B	6.94	2.38	9.44	4.64	7.01	2.00	1.70	1.79	5.52
Elemental Concentrations (µg/L)									
Ni	14.2	10.3	64.2	17.6	8.99	4.82	4.67	5.91	334
Zn	95.9	34.43	278	144	127	37.5	26.6	43.4	354
Zr	1.24	0.58	1.87	2.55	1.48	0.56	0.90	1.27	1.49
Al	11.1	9.10	20.3	7.14	8.06	7.34	4.11	9.56	1238
Th	0.01	n.d	0.04	0.02	0.03	0.05	0.01	0.01	0.02
U	29.13	0.61	21.9	27.15	9.97	5.52	2.55	2.71	34.10
Li	4.71	37.43	103	20.82	8.04	6.45	7.96	10.69	243
Co	0.65	0.46	16.4	1.08	0.49	0.44	0.24	0.98	245
Cu	30.75	17.5	83.4	38.40	14.49	8.14	7.83	12.03	65.87
As	54.76	21.1	87.4	74.60	5.90	18.54	16.35	19.97	46.93
Se	103.2	34.55	177	176	37.7	37.34	33.35	40.38	147
Cd	0.09	0.77	1.14	0.24	0.74	0.74	0.67	0.90	12.2
Ba	40.2	28.38	79.8	26.6	12.3	34.2	44.1	40.7	33.4
Mn	1.82	8.36	6773	2.26	3.71	10.10	2.23	4.62	672

n.d = not detected

CHAPTER 5

Discussion

5.1 Pond samples

The raw effluent is generated during the leachate process where sulphuric acid is used to remove the iron bearing coating found on some zircon grains (*pers. comm.* Halbich, 2003). Lime is added to the raw effluent in order to neutralize it. The raw effluent is pumped to the adjacent evaporation ponds to evaporate the excess water. A cut off trench was installed in order to retain some of the seepage that occurs at the bottom of the evaporation ponds. The chemical characterization of these ponds is described below.

5.1.1 Water Analyses

The pH and EC results of the pond samples are tabulated in Table 4.1 and plotted given in figure 5.1. The pH range from 1.6 for the raw effluent to 8.3 for the seepage pond. The reason for the acidic nature of the raw effluent is the H_2SO_4 that is used in the mineral treatment process and subsequently added to the raw effluent. The EC values range from 11.21 mS/cm to 29.7 mS/cm. The EC values in the raw effluent and seepage pond are higher than the pond effluent and cut off trench. There exists a correlation between conductivity and total dissolved solids. Major contributions to the higher EC values in the raw effluent and seepage pond are SO_4^{2-}, Na^+, Mg^{2+}, Cl^-, Ca^{2+} and K^+ for the raw eluent. For the seepage pond SO_4^{2-}, Cl^-, Na^+, Mg^{2+}, Ca^{2+} and K^+ contribute to the high EC values.

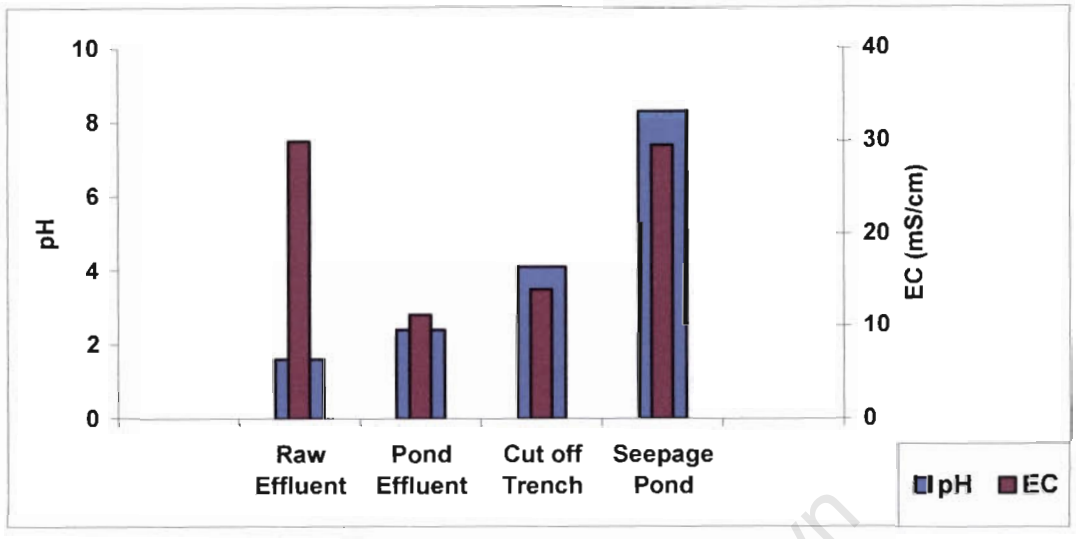

Figure 5.1 pH and EC measurements for four water samples

The pH increases slightly after the addition of lime ($Ca(OH)_2$) with the raw effluent from 1.6 to 2.4 indicating that the neutralizing process is only partially effective. The pH increases in the cut-off trench to 4.1. Towards the seepage pond, the soils act as buffer and the pH rises to 8.3. The pH (1 M KCl) of the soils towards the seepage area (S1-S6) varies from 8.1 – 8.5 except for S2 (5.7). This is indicative that liming material such as $CaCO_3$ with water plays a role in the buffering process, outlined in the reaction below (Sparks, 1995).

$$2Al\text{-soil} + 3CaCO_3 + 3H_2O \rightarrow 3\ Ca\text{-soil} + 2Al(OH)_3 + 3CO_2$$

If we assume from the reaction above that all the acid was neutralised, the pH of the soil would be 8.3 and the soil completely saturated (Sparks, 1995).

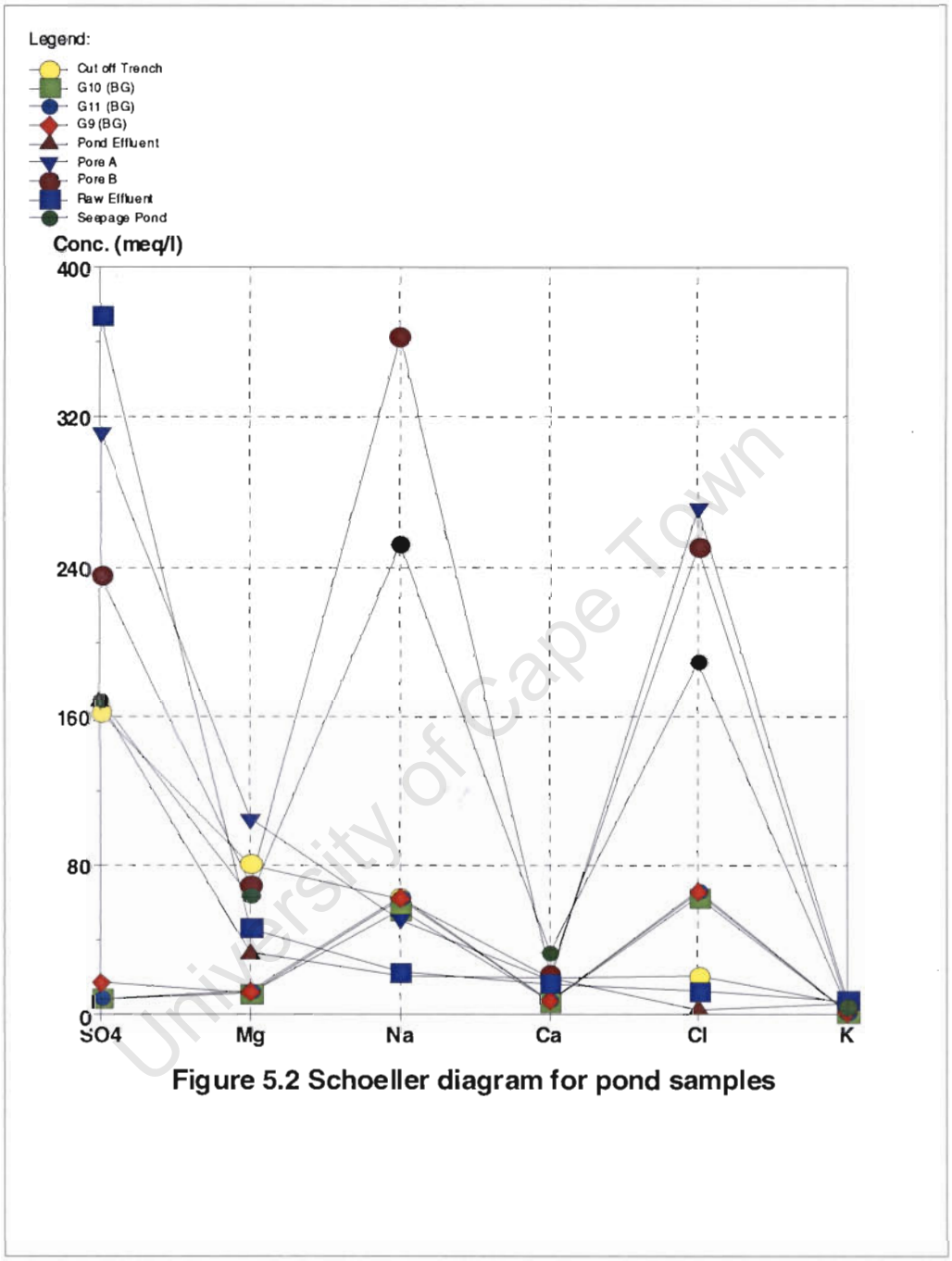

Figure 5.2 Schoeller diagram for pond samples

The major cations and anions of the samples are plotted on an Schoeller diagram (Figure 5.2) to identify different hydrochemical water types on the same diagram.

From the diagram SO_4^{2-} tends to be the most dominant anion for all the samples except for the three background boreholes G9, G10 and G11.The SO_4^{2-} will therefore be a useful tracer to use for the effluent movement. Critto et. al. (2002) used Cl^- and SO_4^{2-} for geostatistical elaboration in their study because they are good indicators for contaminant migration in soils to aquifers. The pore water of the sediment in the seepage pond also display high levels of sulphate. The different water types observed are for the background boreholes as well as for the seepage pond Na-Cl. The raw effluent is SO_4^{2-} dominated due to the sulphuric acid leachate. The pond effluent displays a Mg-SO_4 watertype. The background boreholes also display higher values of Na and Cl compared to the raw effluent. The Na and Cl for all the other boreholes also exceed the raw effluent concentration. The increase in ion concentration in these boreholes will be due to either evaporation or dissolution of minerals or salts.

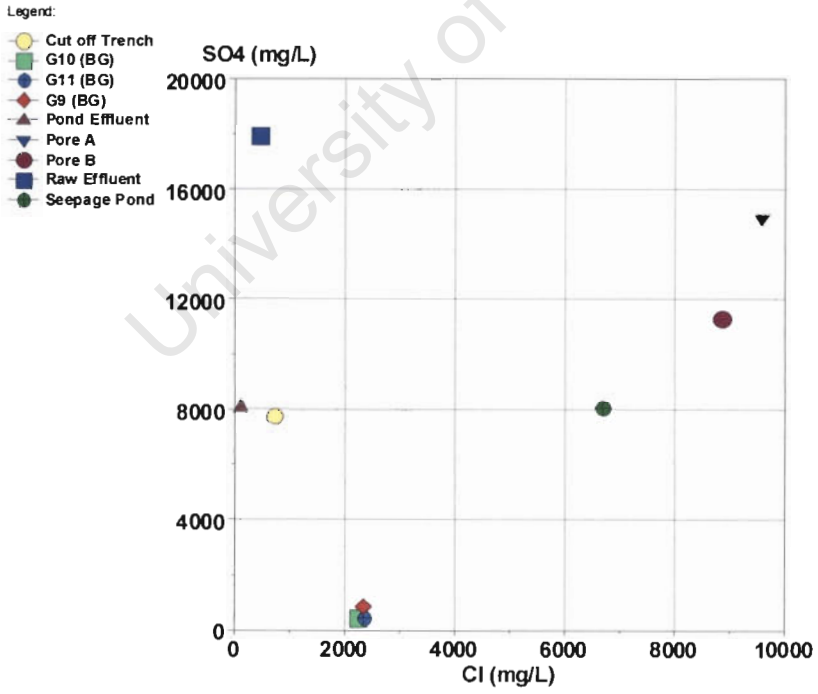

Figure 5.3 Relationship between SO_4^{2-} and Cl^-

From the scatter plot in figure 5.2 it can be seen that the water in the cut-off trench and seepage pond is influenced by the high SO_4^{2-} concentration in the raw effluent.

ICP-MS analysis listed in Table 4.1 reveals elevated concentrations with respect to the present irrigation water guidelines of various metals for the samples analysed (DWAF, 1996). The overall elemental concentrations decrease as it moves to the seepage pond. Indicating retention, either in the gypsum precipitates forming in the ponds or onto the soils. Another possibility that these contaminants might co-precipitate with iron. For the raw effluent Al, Ti, Fe, U, As and Se exhibit high concentrations. The evaporation pond shows lower concentrations for the above elements. The cut-off trench shows elevated levels of B, Al, Mn, Ni U, and Se compared to the DWAF water guidelines for irrigation.

The speciation of the water samples was modeled using PHREEQC. The speciation of ions in the water samples will not be discussed, however the species predicted by PHREEQC for the water samples are listed in Appendix H. From the speciation modeling, PHREEQC predicted that calcium, chloride, potassium, sodium, and sulphate occur mostly as free ions. The complete output file is included in Appendix F by way of an example.

Mineral Saturation Indices

PHREEQC was also used to calculate the saturation of samples with respect to certain minerals that occur in the different samples. Saturation indices indicate the saturation state of a mineral with respect to a solution composition. The saturation index (SI) is defined as:

$$SI = \log_{10}(IAP/K_{sp})$$

For a saturation value > 0 over saturated, SI = 0 saturated and SI < 0 undersaturated.

The saturation indices of the samples are listed in Table 5.1

Table 5.1 Saturation Indices (SI) for the pond samples

	Raw Effluent	Pond Effluent	Cut off trench	Seepage pond (SP)	SP Pore Water A	SP Pore Water B
Mineral				SI		
$Al(OH)_3$ (a)	-9.00	-7.10	-2.58	-3.15	-0.50	0.06
Alunite - $KAl3(SO_4)_2(OH)_6$	-4.69	-0.85	8.02	-6.34	6.45	7.60
Anglesite - $PbSO_4$	-0.43	-1.16	-3.17	-5.27	-2.57	-2.62
Anhydrite - $CaSO_4$	-0.35	-0.40	-0.31	-0.11	-0.17	-0.22
Aragonite – $CaCO_3$	-	-	-	1.30	-	-
Barite - $BaSO_4$	1.58	1.62	0.60	0.54	0.97	1.07
Calcite – $CaCO_3$	-	-	-	1.45	-	-
Celestite - $SrSO_4$	-0.14	-0.63	-0.12	-0.14	0.09	0.03
Chalcedony - SiO_2	-0.38	-0.06	0.44	-0.40	0.33	0.25
Gibbsite - $Al(OH)_3$	-6.35	-4.37	0.17	-0.37	2.28	2.84
Goethite - FeOOH	-5.10	-3.34	-1.28	8.76	6.74	6.68
Gypsum $CaSO_4: 2H_2O$	-0.15	-0.17	-0.07	0.13	0.07	0.02
H_2O (g)	-1.41	-1.63	-1.70	-1.77	-1.77	-1.78
Hematite – Fe_2O_3	-8.18	-4.69	-0.58	19.48	15.45	15.33
Melanterite - $FeSO_4: 7H_2O$	-1.78	-2.03	-4.78	-7.21	-4.92	-5.20
Quartz - SiO_2	0.04	0.38	0.89	0.56	0.79	0.71
SiO_2 (a)	-1.20	-0.92	-0.42	-1.27	-0.54	-0.63

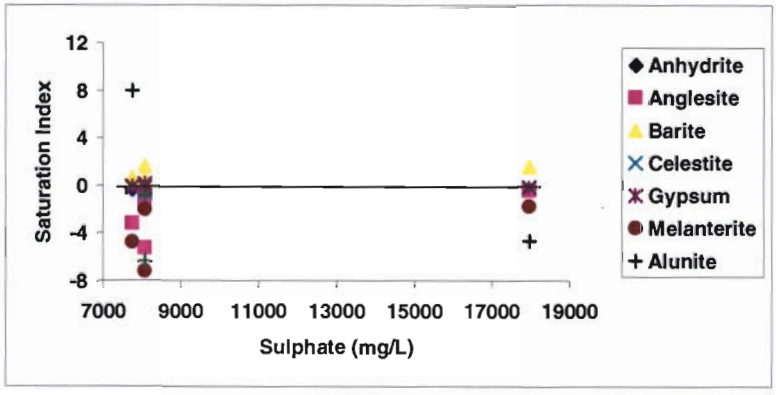

Figure 5.4 Saturation Indices for the pond samples

The water in the seepage pond was found to be supersaturated with respect to the following minerals Aragonite, barite, calcite, goethite, gypsum, hematite and quartz.

5.1.2 Water Quality Assessment

The water quality of the cut off trench will be assessed in terms of the South African Water Quality guidelines for Agricultural Use: Irrigation (DWAF, 1996). The water might be of use to the adjacent land for irrigation purposes and will assist to get rid of the excess waters accumulating in the cut-off trench. Therefore the need to determine its suitability for irrigation. The low pH of 4.1 of the water in the cut of trench excludes it for the use of irrigation. The majority of the ions and metals also exceed the target range as outlined in the DWAF guidelines listed in Appendix G.

5.2 Groundwater

The nine boreholes surrounding the evaporation ponds were sampled to determine if they were impacted from seepage from the evaporation ponds. Boreholes G9, G10 and G11 were sampled as control samples in order to determine the background contaminant level.

General Parameters

5.2.1 pH and EC

The pH and EC measurements taken in the field was similar to the laboratory measurements (Table 4.11). Inspection of Figure 5.5 shows that the pH was observed to be generally between 5.1 for G12 and 7.3 for G4. The boreholes indicate a neutral pH for all except for G12 with the lowest pH of 5.1 that is acidic. The reduction in pH could be due to the close locality of G12 to the evaporation ponds.

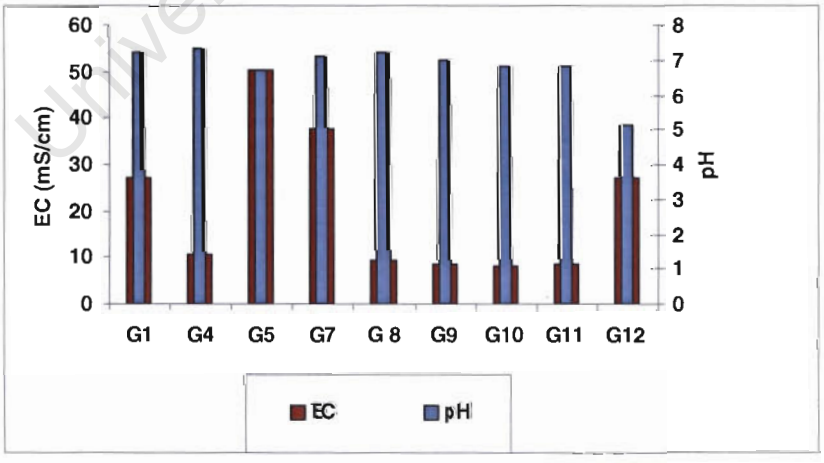

Figure 5.5 pH and EC measurements for the Boreholes

The EC value range between 7.93 mS/cm for G10 and 50.3 mS/cm for G5. Total dissolved salts (TDS) can be calculated from measured EC values (McBride, 1994). The TDS according to Drever (1997) can be used to indicate salinities of water. Drever (1997) classify the waters as follows: Fresh water – less than 1000 mg/L TDS, Brackish waters – 1000 to 20 000 mg/L and Saline waters – similar to or greater than seawater 35 000 mg/L TDS. The borehole water can be describe as brackish except for G5, G7 and G12 can all be described as saline waters.

5.2.2 Redox potential

The oxidation-reduction potential (Eh) measurements were taken in the field. The values range from 86 and 259 mV indicating oxidizing conditions.

5.2.3 Major Ion Chemistry

For all the boreholes, Cl and then Na are the most dominant ions present, except for G8 where the sulphate anion is the dominant ion. It is then followed by sulphate and magnesium except for G4 and G9 where calcium is more dominant than sulphate. For all the major cations and anions in all the boreholes, elevated levels are occurring with respect to the background boreholes. Except for G8 where only Cl^- is less than the background samples. It is also clear that the concentrations of major cations and anions in general have been increased due to infiltration of effluent seepage.

The clustering of the data on the piper diagram can be seen in Figure 5.6. From inspection, in the cation ternary diagram two clusters can be recognized with samples G1 and G8 as one cluster and the other samples as another cluster. For the anion, ternary diagram the clustering is not so clearly defined. The reason might be the dominance by the chloride concentration in all of the samples. In the quadrilateral diagram of the piper plot G1 and G8 forming one cluster and the rest of the other samples another cluster.

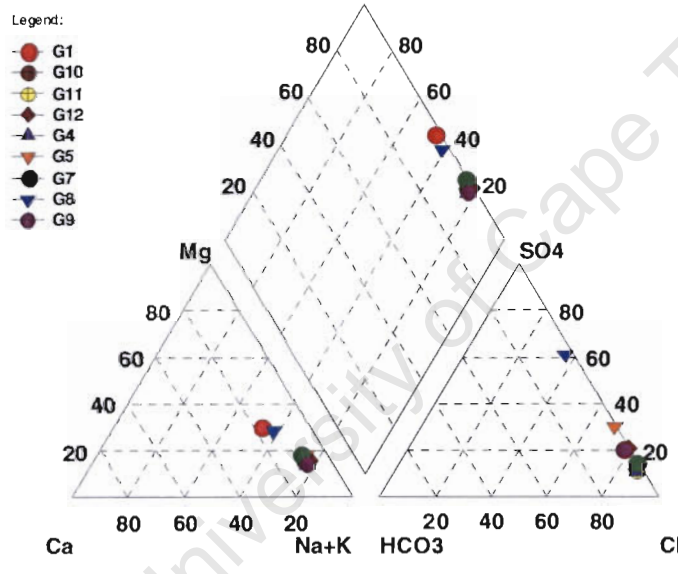

Figure 5.6 Piper trilinear diagram indicating cations and anions for Boreholes

Sodium

The concentration of sodium with values higher than 69 mg/L in water can be considered toxic to crops and this toxicity is related to the concentration of calcium in the water or soil (Evangelou, 1998). For all the boreholes sodium is the most dominant cation present and closely relate to chloride for most of the samples except for G5, G7, G8 and G12. There exist a linear relationship (R^2 = 0.98) between Na^+ and Cl^- (Figure 5.7), and the ratio of boreholes are very similar to that of seawater except for G8, G12, G7 and G5. (Figure 5.8) (Langmuir, 1997). This indicates that there is a strong marine influence on the natural chemistry of these the boreholes.

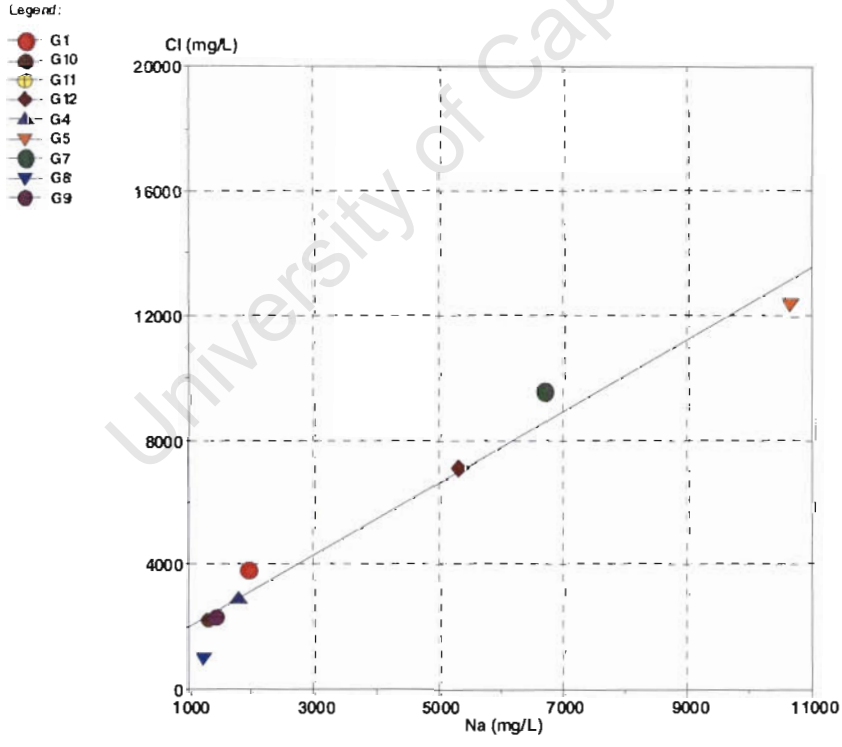

Figure 5.7 Relationship between Na and Cl

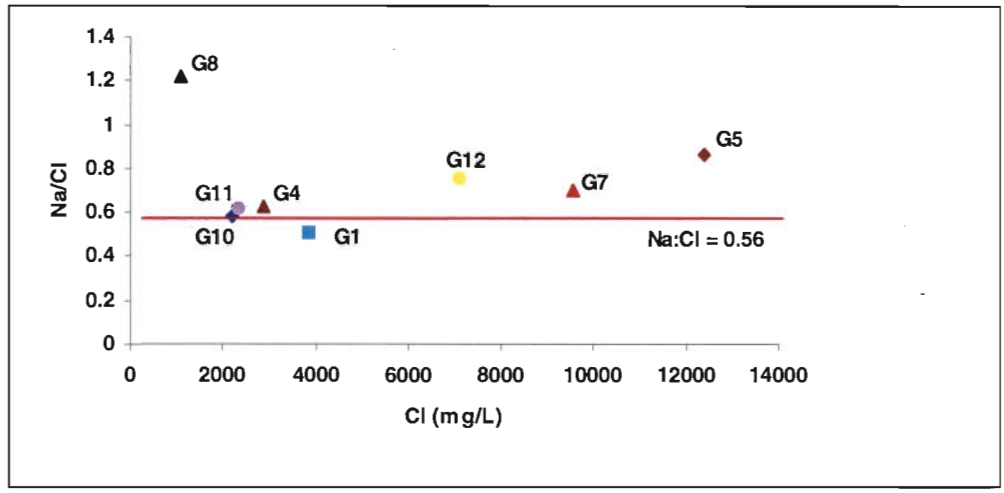

Figure 5.8 Na/Cl ratio. The line indicating Na:Cl ratio in seawater of 0.56 (Langmuir, 1997).

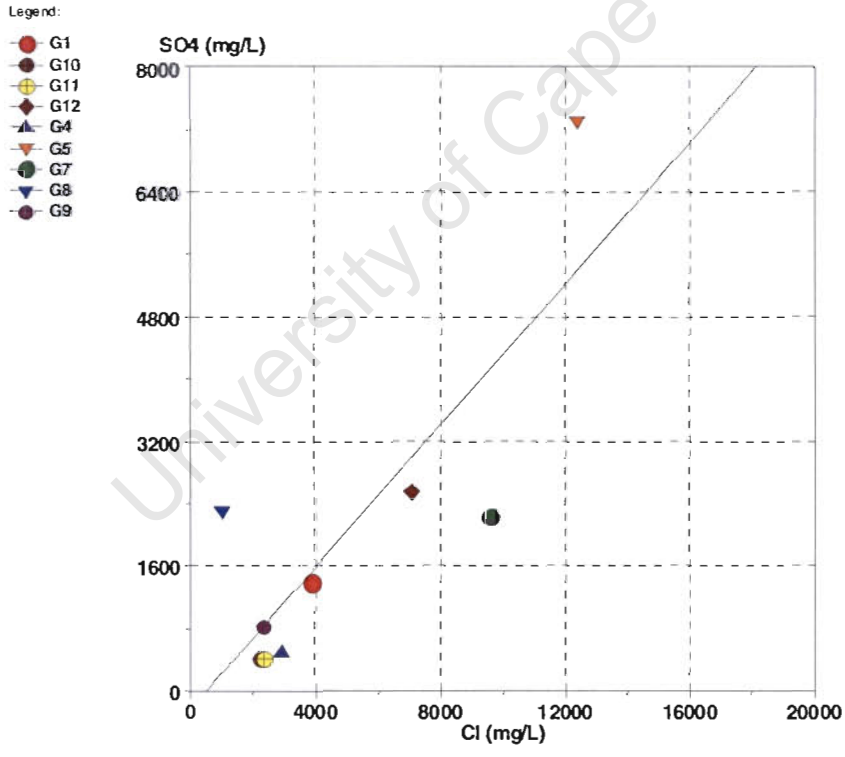

Figure 5.9 Relationship between SO_4 and Cl

Sulphate

In contrast to Na^+ versus Cl^- values, the Cl^- versus SO_4^{2-} do not give a linear relationship for most of the boreholes. All the boreholes except for G10 and G11 shows elevated levels of sulphate in relation to SO_4^{2-} Cl ratio (0.14) for seawater (Langmuir, 1997). This elevation is indicative of anthropogenic contamination.

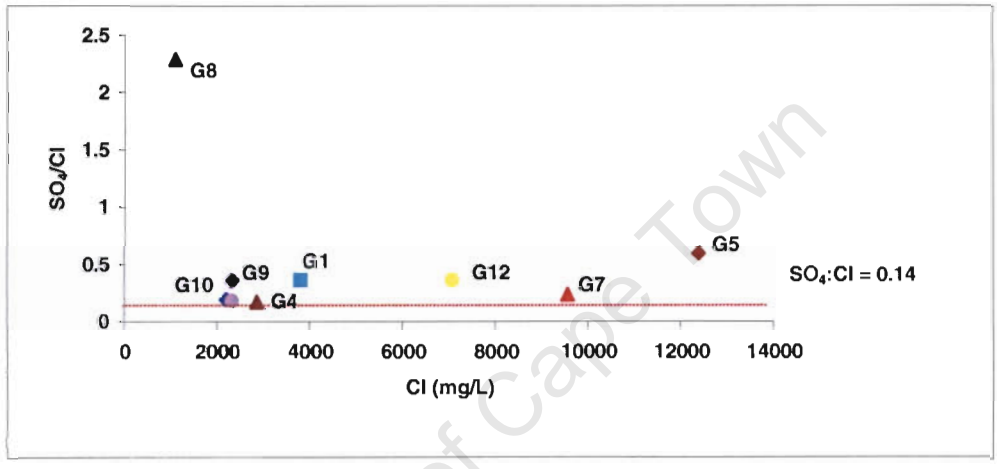

Figure 5.10 SO_4/Cl ratio. The line indicating SO_4:Cl ratio in seawater of 0.14 (Langmuir, 1997).

5.2.4 Chemical Speciation

PHREEQC was used to do speciation calculations for the borehole samples collected. The chemical species predicted by PHREEQC are tabulated in Appendix H. From the speciation modeling, PHREEQC predicted that calcium, chloride, potassium, magnesium, sodium and sulphate occur mostly as free ions.

Table 5.2 Saturation Indices (SI) for the Groundwater Samples

	G 1	G 4	G 5	G7	G 8	G 9	G10	G11	G12
Mineral									
Al $(OH)_3$ (a)	-1.81	-1.87	-1.12	-0.92	-1.93	-1.97	-2.20	-1.81	-2.45
Alunite - $KAl3(SO_4)_2(OH)_6$	-0.76	-2.28	3.89	2.24	-0.62	-1.09	-1.76	-0.75	3.93
Albite – $NaAlSi_3O_8$	0.22	-0.64	1.28	0.49	0.19	-0.62	-0.75	-0.35	-2.87
Anhydrite - $CaSO_4$	-0.65	-1.33	-0.16	-0.58	-0.64	-1.18	-1.44	-1.44	-0.65
Aragonite – $CaCO_3$	0.25	0.02	-0.34	0.02	-0.15	-0.44	-0.69	-0.76	-2.53
Barite - $BaSO_4$	0.21	-0.09	0.76	0.00	-0.02	0.21	0.12	0.04	0.25
Calcite – $CaCO_3$	0.39	0.17	-0.20	0.16	-0.01	-0.30	-0.55	-0.62	-2.38
Celestite - $SrSO_4$	-0.86	-1.45	-0.22	-0.71	-0.82	-1.44	-1.62	-1.64	-0.66
Chalcedony - SiO_2	0.19	-0.10	0.24	-0.16	0.16	0.07	0.18	0.17	-0.07
Dolomite – $CaMg(CO_3)_2$	1.14	0.61	0.17	0.78	0.40	-0.29	-0.77	-0.91	-4.29
$Fe(OH)_3$ (a)	2.97	2.55	1.89	3.00	2.67	2.16	2.15	2.14	0.05
Gibbsite - Al $(OH)_3$	0.90	0.84	1.60	1.79	0.78	0.75	0.52	0.90	0.27
Goethite - FeOOH	8.77	8.33	7.67	8.82	8.47	7.95	7.94	7.95	5.84
Gypsum $CaSO_4$: $2H_2O$	-0.43	-1.10	0.05	-0.37	-0.41	-0.95	-1.21	-1.21	-0.43
H_2O (g)	-1.58	-1.59	-1.60	-1.57	-1.58	-1.58	-1.58	-1.57	-1.59
Hematite – Fe_2O_3	19.53	18.65	17.35	19.64	18.94	17.91	17.87	17.90	13.68
Jarosite-K – $KFe_3(SO_4)_2(OH)_6$	3.27	0.61	2.51	3.75	2.90	0.98	0.93	0.85	1.07
K-feldspar – $KAlSi_3O_8$	1.55	0.19	1.90	1.21	1.06	0.36	0.25	0.53	-2.13
Melanterite - $FeSO_4$: $7H_2O$	-7.78	-8.40	-5.14	-7.15	-7.28	-7.56	-7.85	-8.13	-5.57
Quartz - SiO_2	0.63	0.34	0.68	0.28	0.60	0.51	0.62	0.60	0.37
SiO_2 (a)	-0.66	-0.95	-0.61	-1.01	-0.69	-0.78	-0.67	-0.68	-0.92

5.2.5 Mineral saturation indices

For the selected samples a large portion of the sulphate minerals, specifically Melanterite, Celestite and anhydrite, as well as $Al(OH)_3$ (a) and SiO_2 (a) are undersaturated. Supersaturated samples have a positive saturation index where a mineral phase is expected to precipitate out of solutions. For the samples the following minerals are supersaturated, $Fe(OH)_3$ (a), Gibbsite, Goethite, Hematite, Jarosite-K, K-feldspar and Quartz. Hematite (Fe_2O_3) displays quite high S.I values of between 13.68 and 19.64. Saturation indices of approximately zero imply that the sample is in equilibrium with a particular mineral phase, which should, therefore, neither precipitate nor dissolve which is the case for Gypsum that show values close to equilibrium for all the samples.

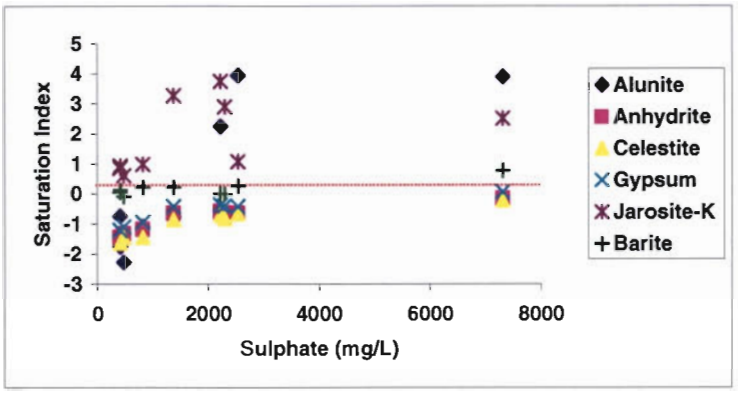

Figure 5.11 Saturation indices for borehole samples

5.2.6 Trace elements

Uranium

Elements like uranium, selenium, arsenic and molybdenum, are soluble under oxidizing conditions in groundwater (Drever, 1997). The boreholes under investigation all shows oxidizing conditions based on the Eh measurements. The levels of uranium in the different boreholes are plotted below in Figure 5.12. Only G4 is lower than the control samples, all the other boreholes show elevated levels of uranium. From the spatial distribution map Figure 5.13 the uranium plume increases in the direction of G1 and G12.

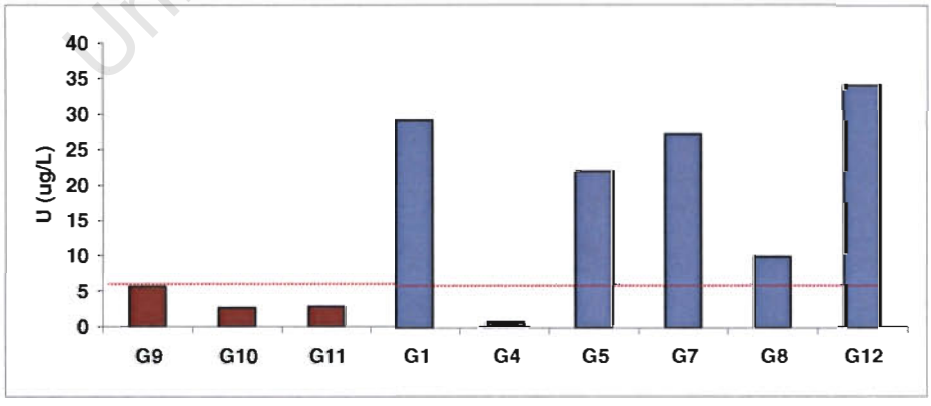

Figure 5.12 Uranium levels in boreholes

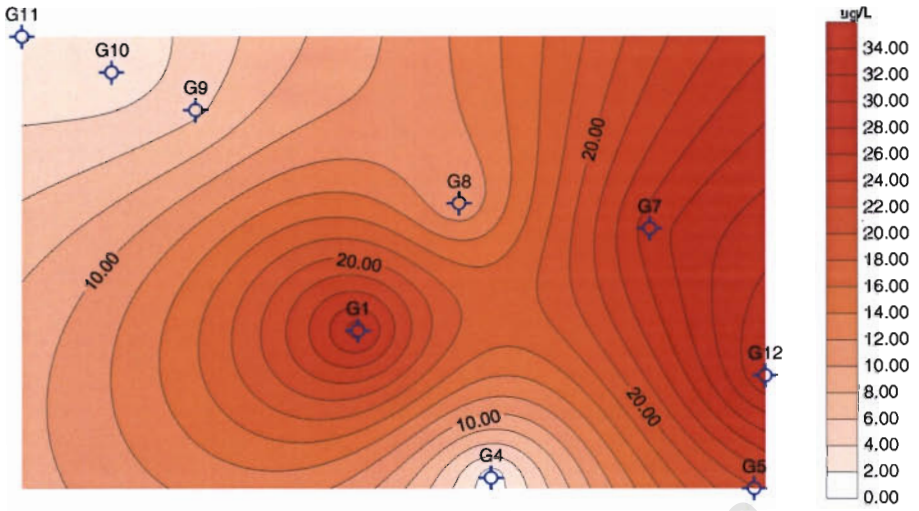

Figure 5.13 Spatial distribution map of Uranium

Arsenic

For arsenic and selenium under oxidizing conditions arsenic mainly occurs in the +V oxidation state and selenium as selenate (Drever, 1997). Arsenic in groundwater normally contains arsenite and arsenate, arsenate is more toxic than arsenate (Chatterjee et, al. 1992). For arsenic only G8 shows levels less than the control samples, all the other boreholes are elevated with respect to the control samples. For the spatial distribution of arsenic the plume is mainly moving in the direction of G5.

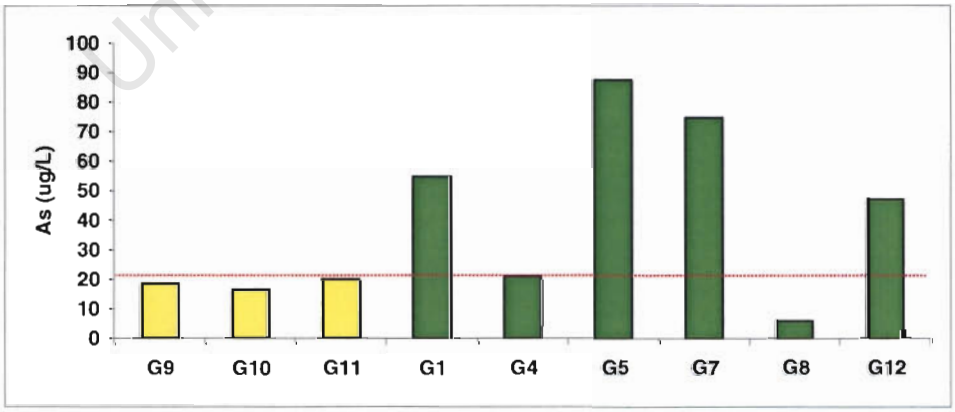

Figure 5.14 Arsenic levels in boreholes

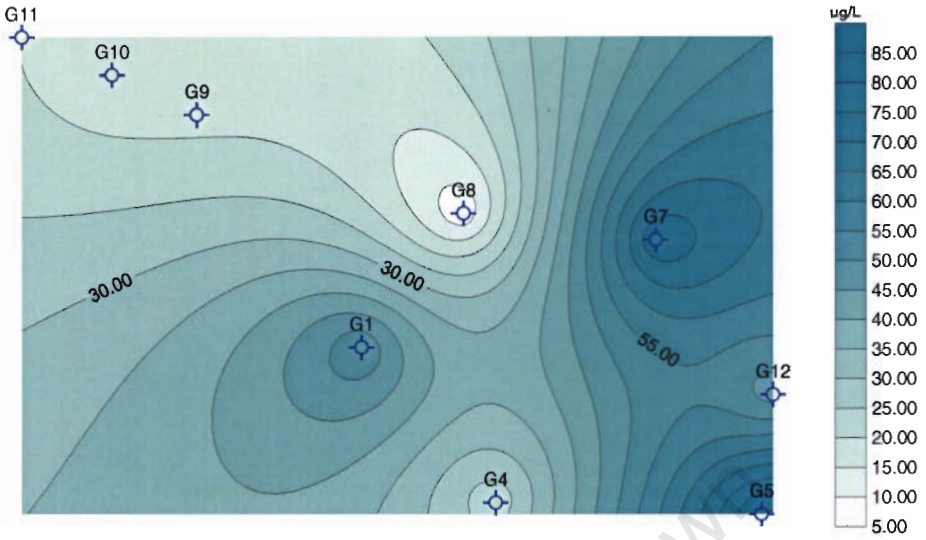

Figure 5.15 Spatial distribution map of Arsenic

Selenium

For Selenium only G4 shows levels less than the control samples, all the other boreholes are elevated with respect to the control samples. G8 shows similar levels than G11 that is one of the background boreholes. For the spatial distribution of arsenic the plume is mainly moving in the direction of G5. The plume distribution is also towards G5.

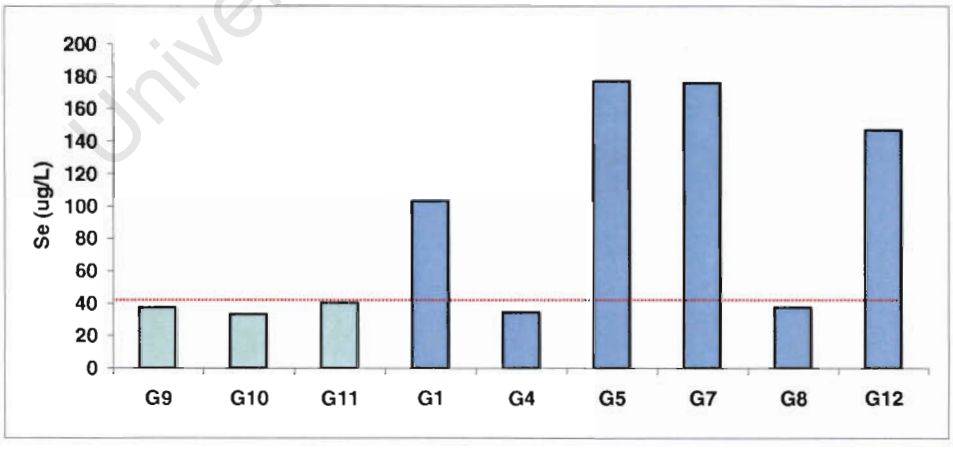

Figure 5.16 Selenium levels in boreholes

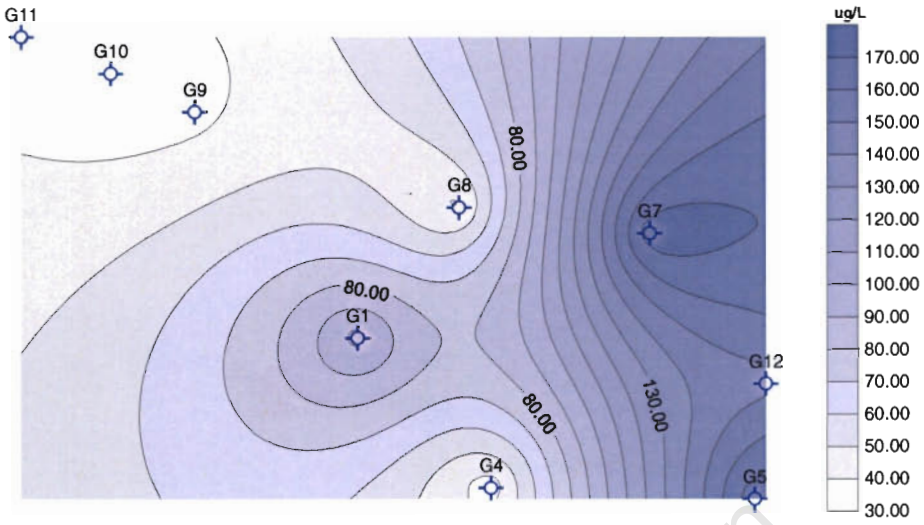

Figure 5.17 Spatial distribution map of Selenium

Sulphate

The sulphate concentration for the boreholes displayed is all higher than the background boreholes except for G4 with more or less the same concentration. The highest sulphate levels occur in G5.

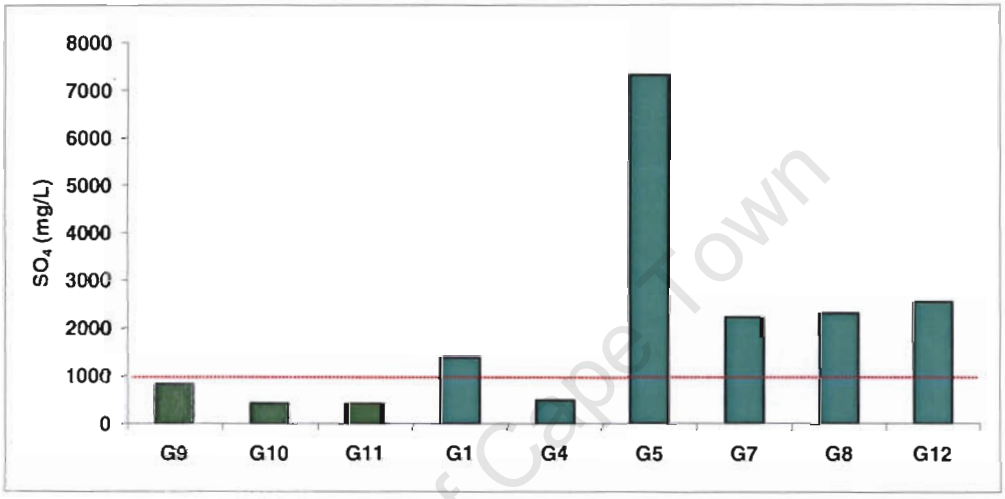

Figure 5.18 Sulphate levels in boreholes

Figure 5.19 Spatial distribution map of Sulphate

Silicon

The results of the two methods show some correlation between the two methods except for G9, where the results of the ICP-MS are much lower. The values obtained from the colorimetric method were used in plotting the spatial distribution of silicon. Silica content in groundwaters is normally high due to the active degradation of silicate minerals (Appelo and Postma, 1994). From the spatial distribution map the increase in silicon concentration is basically towards the background boreholes.

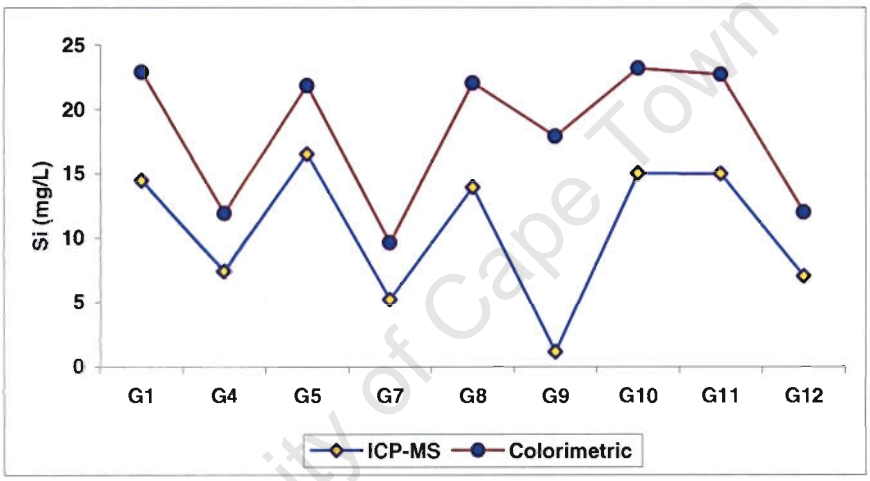

Figure 5.20 Comparison of Si concentration determinations by ICP-Ms and Colorimetric method

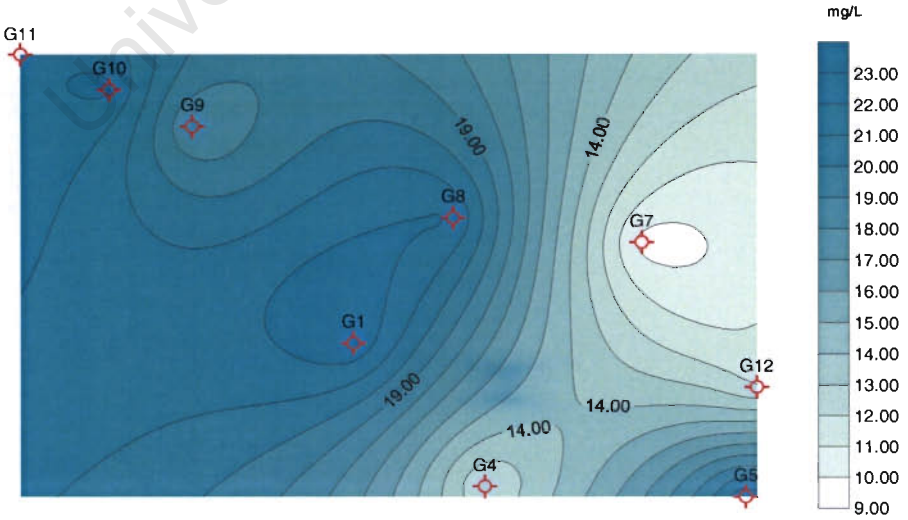

Figure 5.21 Spatial distribution map of Silicon

5.2.7 Water Quality Assessment

The water quality of the boreholes will be assessed in terms of the South African Water Quality guidelines for Agricultural Use: Irrigation and Livestock watering (DWAF, 1996). It will also be compared to the guidelines outlined in Evangelou, (1998) to assess if the borehole waters will be suitable for irrigating crops in the area. The water quality for most of the boreholes around the evaporation ponds is not suitable for domestic use.

Irrigation

The guidelines for the interpretation of the water quality of the boreholes for the use of irrigation purposes on crops are tabled below Table 5.3.

Table 5.3 Guidelines for Interpretation of Water Quality for Irrigation (from Evangelou, 1998)

Irrigation Problem	Degree of Problem		
	No Problem	Increasing Problem	Severe Problem
Salinity (affects water availability to crop)			
[1]EC_W (mS/cm)	< 0.75	0.75 – 3.0	> 3.0
Specific toxicity (affects only sensitive crops)			
Sodium (SAR)	< 3	3 - 9	> 9
Chloride (meq/L)	< 4	4.10	> 10
Boron (mg/L)	< 0.5	0.5	2.0 – 10.0
Miscellaneous effects (affects only from susceptible crops)			
HCO_3 (meq/L)	< 1.5	1.5 – 8.5	> 8.5
pH		Normal Range 6.5 – 8.4	

[1]EC_W = electrical conductivity

[2]SAR: = adjusted sodium adsorption ratio

Table 5.4 Assessing Borehole Water Qualities for Irrigation

	Boreholes								
Irrigation Problem	G1	G4	G5	G7	G8	G9	G10	G11	G12
Salinity									
[1]EC_W (mS/cm)	27.2	10.6	50.3	37.5	9.2	8.4	7.9	8.42	27.0
Specific toxicity									
Sodium (SAR)	13.5	22.7	52.2	39.5	12.0	20.0	18.2	19.9	39.6
Chloride (meq/L)	108.1	81.0	349.7	269.9	28.5	65.5	62.6	65.9	199.9
Boron (mg/L)	6.9	2.4	9.4	4.6	7.0	2.0	1.7	1.8	5.5
Miscellaneous effects									
HCO_3 (meq/L)	3.79	4.1	4.2	3.1	3.3	3.6	3.0	2.4	1.3
pH	7.2	7.3	6.7	7.1	7.2	7.0	6.8	6.8	5.1

[1]EC_W = electrical conductivity
[2]SAR: = adjusted sodium adsorption ratio
b.d.l = below detection limit
Severe problem
Increasing problem

The irrigation water salinity (EC_W) of the boreholes will cause severe problems if it must be used for the irrigation of crops in this area. Sodium and chloride will also cause severe problems. For boron only G10 and G11 shows an increasing problem while all the other boreholes show the same trend as above. The pH range for the boreholes is quite normal except for G12 that displays a low pH of 5.1.

Sodicity – salinity relationship

Evangelou, (1998) classifies waters with an EC higher than 8 mS/cm as very high saline waters and a sodium hazard with a SAR value higher than 26 also very high. All the borehole waters can be classified as very high saline waters (Evangelou, 1998). The sodium hazard for G5, G7 and G12 are classified very high, G11, G10, G9 and G4 high and G1 and G8 medium (Evangelou, 1998).

The majority of the ions and metals also exceed the target range as outlined in the DWAF guidelines listed in Appendix G. therefore these waters can not be used for irrigation purposes or livestock watering in this area.

5.3 Pond precipitate samples

5.3.1 Bulk chemical and mineralogical analysis of pond precipitate samples

For the bulk, chemical analysis for the two gypsum precipitate samples in the ponds all the elements except for sodium in sample S21 are much higher than the background levels in the soil. These precipitates therefore retain many of the contaminants present in the raw effluent entering the ponds. The precipitate forming on the soil surface reveals elevated levels for the following elements, Na, Mg, Sr, U and Zr with respect of the background soil levels. The X-ray diffractograms of the three different precipitates are shown in Figure 4.1 and 4.2. The precipitate samples in Figure 4.1 mainly show gypsum. The gypsum is formed upon precipitation during the liming of the raw effluent. Figure 4.2 displays the precipitate forming on the soil surface could not be identified and were identified as a hydrated sulphate mineral. Based on the bulk analysis of this sample sodium displays the highest concentration of the elements analysed. Therefore the possibility of the precipitate to be either Thenardite (Na_2SO_4) or Mirabilite ($Na_2SO_4 \cdot 10H_2O$).

5.4 Soil Chemistry

The soils around the evaporation ponds were chemically characterised to determine the effect of the seepage from the evaporation ponds on it. Samples from three horizons were collected from soil not affected by the seepage to serve as background levels.

5.4.1 Soil Acidity

Evangelou, (1998) classifies soil acidity into three types as follows: i) Soluble and exchangeable acidity (Al^{3+} plus H^{+}), ii) Titratable acidity (soluble and exchangeable Al^{3+} plus H^{+} and nonexchangeable Al-hydroxy or Fe-hydroxy polymers), iii) Total acidity, refers to titratable acidity up to pH 8.2 which includes H_3O^{+} in the pH range < 4, Al^{3+} in the range of 4 – 5.6, strong aluminium hydroxy in the pH range 5.6 – 7.6, and weak aluminium – hydroxy in the pH range greater than 7.6 (Evangelou, 1998).

Hydrolysis is normally the process responsible for soil acidification, and the most common element associated with this process is Al^{3+} (Evangelou, 1998). Evangelou, (1998) describes it as, where the aluminium ions on mineral surfaces hydrolyze to produce H^{+}, which in turn attacks the clay surfaces to produce more acidity (Evangelou, 1998).

$$Al^{3+} + nH_2O \Leftrightarrow - Al(OH)_n^{(3-n)} + nH^{+}$$

It is therefore, necessary to consider acidity as a critical characteristic that will strongly influence soil behaviour.

5.4.2 Soil pH

The pH of the samples were measured in MilliQ H_2O, 1M KCl and in the saturated paste extracts. The pH measured in water for the various sample ranges from 4.8 for S9, strongly acidic (Soil classification working group, 1991) to 9.5 for S4, strongly alkaline. Soil pH values below 5.0 to 5.5 warn that soluble levels of certain metals, particularly Al^{3+} and Mn^{2+}, may be high enough to be biologically toxic (McBride, 1994) which is the case for sample S9. Tan (1994), states that soil in arid regions is normally characterized by a pH of 7.0 to 9.0 in the surface soil. The reason for this pH range is because adsorbed bases are not leached away and the soils will remain saturated with bases.

It was necessary to measure the pH in a solution of KCl solution because it gives a more realistic idea of the pH that affects ions in solution. The K^+ ions exchange for H^+ and Al^{3+} ions on exchange sites, resulting in a lower pH in solution than will be measured in distilled water. The difference between pH_{H2O} and pH_{KCl} (ΔpH_{KCl}) varies from –0.4 for sample S3 to –1.4 for sample S4. The pH values taken in the saturated paste extracts range from 5.0 for S9 to 8.5 for S4 lower than those taken in MilliQ H_2O.

The relationship between pH (H_2O) and pH (KCl) shows a consistent change therefore a linear relationship with a slope of 0.987 and a y-intercept of 0.57, reveals, on average the ΔpH_{KCl} is 0.6.

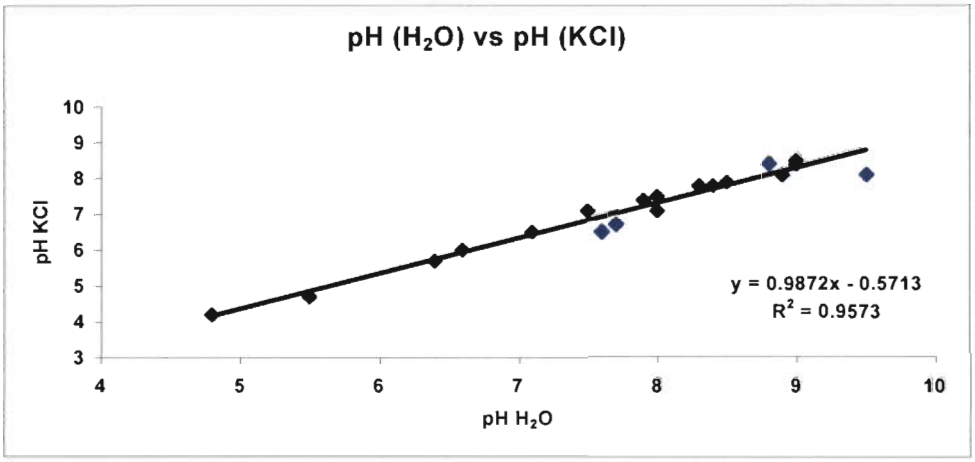

Figure 5.21 pH (H_2O) vs pH (KCl)

The lower pH values observed in the pH (KCl) are expected as the use of 1 M KCl will result in a higher amount of exchangeable H^+ and Al^{3+} being displaced than with the use of MilliQ water. According to Alloway (1995) the pH value obtained is about 1 to 1.5 units higher than that of the soil solution near to the solid surfaces where the reactions take place.

In general, the soil samples for the background levels A-C and S1-S6 can be considered to be moderately alkaline except for S2 moderately acidic. Sample S9 and S29 can be considered as strongly acidic. The reason for the strong acidity of S9 might be of its close location to the evaporation ponds.

5.4.3 Exchangeable acidity

The acidity measured as the moles titrable protons per unit mass displaced by an unbuffered KCl solution are termed the exchangeable acidity. Exchangeable acidity is composed of four types of acidity. The first is the H ions obtained from the hydrolysis of exchangeable, trivalent Al.

The second is from hydrolysis of partially hydrolysed and non-exchangeable Al. The third type is from weakly acidic groups, mostly organic matter, and the fourth is exchangeable H (Evangelou, 1998). The only sample with a significant extractable acidity is sample S9 (29.5 $mmol_c$ /kg). The other samples are much lower in the range of less than 1.2 $mmol_c$/kg.

5.4.4 Base saturation

The cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) are known as basic, or (H^{+}, Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^{+}$) which are known as acidic cations, is balanced by the negative charge on clay and humus (Wild, 1994). Base saturation refers to the percentage of cations exchange sites occupied by basic cations. For the samples, only Mg^{2+} and Ca^{2+} and exchangeable acidity were used to calculate the base saturation for selected soil samples listed in Table 4.3. For all the samples a high base saturation was observed which according to Tan, (1993) is normal in an arid region and these soils is normally higher than soils in humid regions. The reason for this is the concentration of salts at the surface by evaporation.

5.4.5 Salinity

The measured EC values for the samples are tabulated in Table 4.4. According to McBride (1994) EC values greater than 4 mS/cm are indicative of saline conditions. All the measured values listed in table 4.4 are greater than 4 mS/cm. Therefore all saline including the natural samples.

Table 5.5 Characterization of Saline and Sodic Soils and its potential to degrade soil properties (Adapted from McBride, 1994)

Soil Properties	EC (mS/cm)	ESP (%)	Typical pH	Structure
Saline	> 4	< 15	< 8.5	Good
Sodic	< 4	> 15	> 9.0	Poor
Sodic-saline	> 4	> 15	< 8.5	Fair-good
Solution Properties				
Hazard	Salinity (EC)	Sodicity (SAR)	Alkalinity	
Low (safe)	< 0.25	< 7	< 1.25	
Medium (marginal)	0.25 – 0.75	7 – 13	1.25 – 2.5	
High (unsuitable)	0.75 – 2.25	13 – 20	> 2.5	
Very high	> 2.25	> 20	> 2.5	

5.4.6 Sodicity

From the table above the samples can all be classified as saline-sodic soils except for S2. Saline – sodic soils have an EC > 4 mS/cm and an ESP > 15. Thus, both soluble salts and exchangeable Na^+ are high in these soils. Since electrolyte concentration is high, the soil pH is usually < 8.5 and the soil is flocculated (Sparks, 1995).

5.4.7 Soil water elemental composition

Analysis of the soil solution is an appropriate measure of elemental availability, because it will measure the concentration of soluble elements in the soil solution available to plants.

5.4.8 Major cations and anions

The proportions of major cations and anions of some of the soil solution samples are plotted in the Piper trilinear diagram in Figure 5.22. From the diagram SO_4^{2-} and Cl^- are the most dominant ions for the samples plotted but there is no dominant cation type for most of the soil solution samples, except for C1 and C2, which are dominated by Mg^{2+} and Na dominated for samples B, S28, S29, S27, S30, S26 and S25 Whereas for the major anions, almost all the soil solution samples indicates a trend to be Cl^- dominated. Except for S4 and S9 to be SO_4^{2-} dominated.

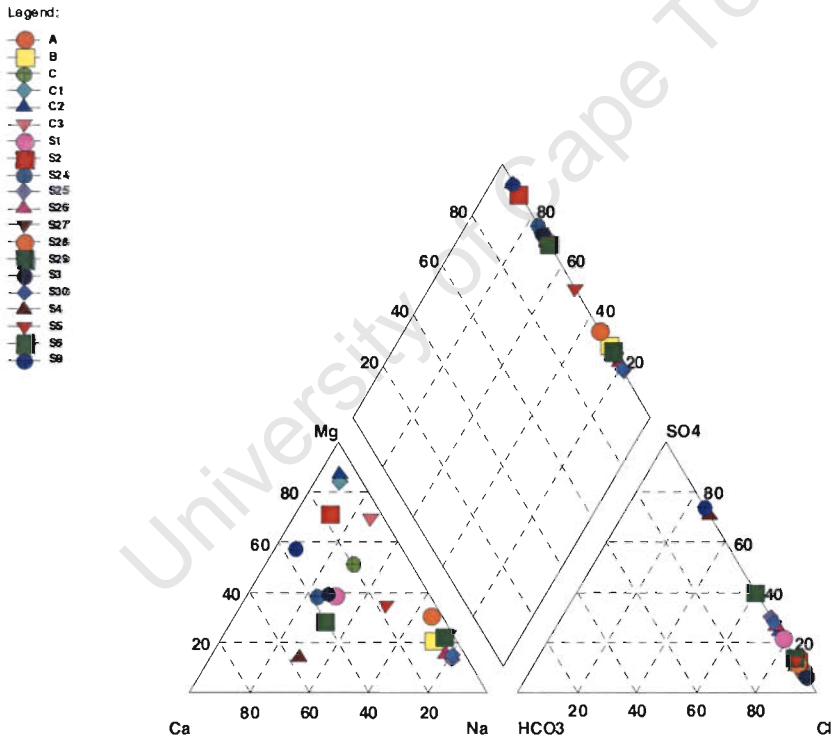

Figure 5.22 Piper trilinear diagram indicating major cations and anions for soil solution.

5.4.9 Micronutrients and other trace elements

The nutrients required for plant growth fall into two types – the macronutrients (Ca, K, N, P, Mg and S), which are used in relatively large quantities, and micronutrients (Fe, Mn, Zn, cu, Cl, B, Mo) or trace elements, used in relatively small amounts (Ellis and Meller 1995). Plant growth can be retarded if these occur in insufficient quantities, are not balanced by other nutrients or do not become available sufficiently quickly. Micronutrients are required by plants in only small amounts, but they are no less important than macronutrients. For the micronutrients analysed for the soil solution samples, almost all the samples shows elevated levels in relation to the background sample, A.

For samples S2, S23, S24, and S27 the boron concentration are lower than sample A. Boron toxicity is common in alkaline soils of arid regions (McBride, 1994). The manganese in sample S9 is quite higher (49.3 mg/L) in relation to the background sample. Manganese is also a common toxic element in acid soils (McBride, 1994), which corresponds to the acid nature of sample S9. Phytotoxic elements are nickel, cobalt and copper, for the samples analysed some samples shows higher levels of concentration than the background sample, but it do not exceeds the average limits observed for soils worldwide (McBride, 1994).

5.4.10 Chemical Speciation

PHREEQC was used to do speciation calculations for the six water samples collected from the paste extract discussed. The chemical species predicted by PHREEQC are tabulated in Appendix H. From the speciation modeling, PHREEQC predicted that calcium, chloride, potassium, magnesium, sodium, and sulphate occur mostly as free ions.

Table 5.6 Saturation Indices (SI) for the paste extract samples

	B	S 2	S 5	Pore A	S 24	S 25	S 26	S 27	S 28	S29	S 30
Mineral						SI					
$Al(OH)_3$ (a)	-1.3	-1.9	-1.7	-1.3	-2.1	-1.5	-1.4	-0.3	-2.2	-2.0	-1.7
Alunite - $KAl3(SO_4)_2(OH)_6$	1.2	-3.5	-1.5	0.8	-4.4	0.6	1.4	5.5	-3.2	4.9	-0.1
Albite – $NaAlSi_3O_8$	0.8	1.2	0.5	1.4	-0.6	1.4	1.3	2.3	1.0	-0.4	0.2
Anhydrite - $CaSO_4$	-0.3	-0.1	-0.1	0.1	-0.7	-0.5	-0.2	0.2	-0.5	-0.5	-0.2
Aragonite – $CaCO_3$	-	-	-	-	-	-	-	-	-	-	-
Barite - $BaSO_4$	0.3	1.0	0.7	1.1	1.0	0.8	0.8	0.4	-0.2	0.4	1.0
Calcite – $CaCO_3$	-	-	-	-	-	-	-	-	-	-	-
Celestite - $SrSO_4$	-0.2	-0.3	0.2	0.5	-0.9	-0.5	-0.3	0.4	-0.4	-0.3	-0.2
Chalcedony - SiO_2	-0.1	0.3	-0.1	-0.01	-0.1	0.3	0.2	-0.2	0.1	0.4	-0.2
Gibbsite - $Al(OH)_3$	1.4	0.8	1.0	1.4	0.6	1.2	1.3	2.4	0.5	0.7	1.0
Goethite - FeOOH	8.6	9.6	9.4	9.3	9.6	8.4	8.4	7.4	9.2	2.7	8.8
Gypsum $CaSO_4: 2H_2O$	-0.1	0.1	0.2	0.3	-0.5	-0.3	-0.04	0.2	-0.3	-0.3	0.02
H_2O (g)	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.6	-1.5	-1.5	-1.5
Hematite – Fe_2O_3	19.2	21.3	20.9	20.5	21.3	18.9	18.9	16.8	20.4	7.4	19.5
Jarosite-K – $KFe_3(SO_4)_2(OH)_6$	3.2	3.6	4.3	4.9	3.3	2.7	3.2	0.7	3.2	-8.9	3.7
Melanterite - $FeSO_4: 7H_2O$	-5.3	-6.5	-5.9	-6.0	-6.4	-5.4	-5.1	-6.1	-6.3	-5.5	-5.3
Quartz - SiO_2	0.4	0.8	0.3	0.4	0.4	0.7	0.6	0.2	0.5	0.8	0.2
SiO_2 (a)	-0.9	-0.5	-1.0	-0.9	-0.9	-0.6	-0.7	-1.0	-0.8	-0.5	-1.0

5.4.11 Mineral saturation indices

For the selected samples a large portion of the sulphate minerals, specifically Melanterite, Celestite and anhydrite, as well as chalcedony and SiO_2 (a) are undersaturated. Supersaturated samples have a positive saturation index where a mineral phase is expected to precipitate out of solutions. For the samples the following minerals are supersaturated, Alunite, Albite, Goethite, Hematite and Jarosite-K. Saturation indices of approximately zero imply that the sample is in equilibrium with a particular mineral phase, which should, therefore, neither precipitate nor dissolve.

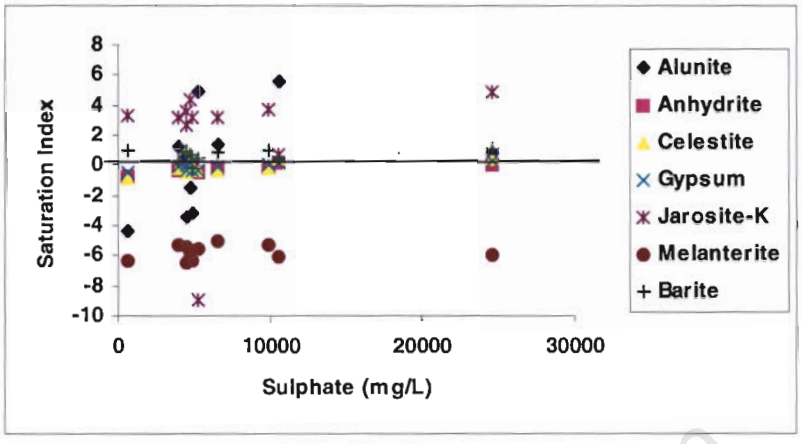

Figure 5.23 Saturation indices for soil solution samples

5.4.12 Bulk mineralogy

The diffractograms of the selected bulk soil samples are shown in Appendix E. the samples are all very similar and displays mainly feldspar and quartz peaks. Feldspar is a good buffering mineral and is important sources of K in soils (Sparks, 1995).

5.4.13 Particle size

The particle size analysis (Table 4.3) for the samples range from 42.3 % - 72.8 % for the sand fraction. The highest clay content occurs in sample S28 and S29 with 29.4% and 19.0 % respectively.

5.4.14 Phosphate sorption isotherm

Phosphate sorption properties of selected soil samples were investigated to determine the availability and uptake of P by measuring the slope of adsorption isotherms (Appendix D). Phosphate also gives a measure of the capacity of soils to sorbs contaminants (*pers. comm.* Smith, 2003). Organic matter and Al/Fe oxides play an important role in P sorption in soils as well as the soil clay content (Atalay, 2001). However, the soils analysed for phosphate sorption displays very low organic content. The total Al and Fe however are quite high. The amount of the P sorbed in soil particles was measured as a function of its concentration in solution. Therefore, if the retention is high the availability to the plants will be low (Foth, 1997). For the selected soil samples sample S30 displayed a lower estimated sorption capacity than the other samples.

5.4.15 Bulk Analysis

Bulk trace elemental composition

The trace element data for the bulk soil samples listed in Appendix B was compared to the background sample A.

Thorium

The concentration for the samples plotted in figure 5.24 are all higher than the background sample A, except for sample S24. Sample S9 displays the highest concentration 19.2 mg/kg. A median value of 9 mg/kg is listed by Sparks, (1995) for soils around the world.

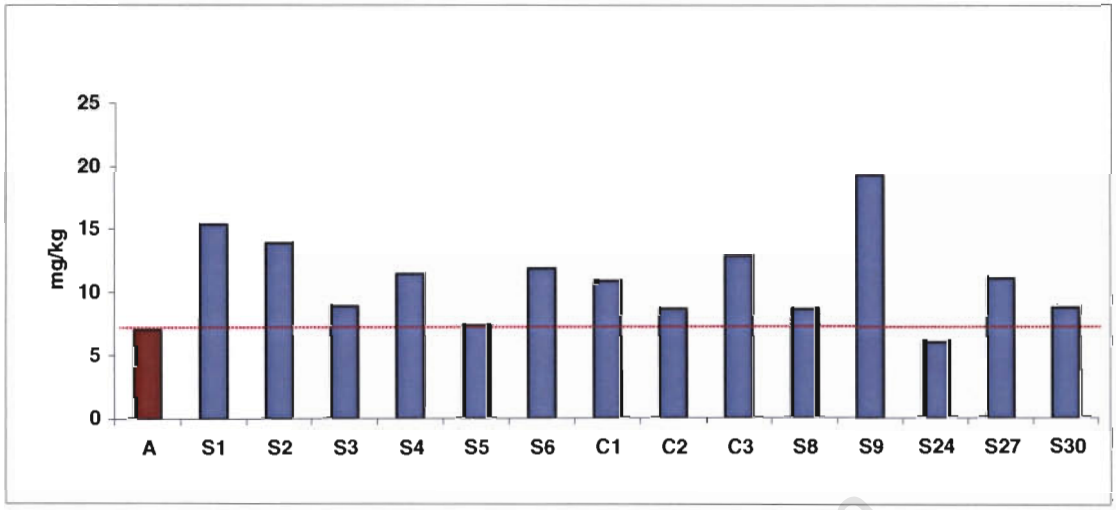

Figure 5.24 Th (mg/kg) in Bulk soil samples

Uranium

For uranium the same trend can be observed as for thorium with samples S9 with the highest and S24 the only sample less than the background sample. The average uranium content of uranium in soils around the world is given as 2 mg/kg (Sparks, 1995).

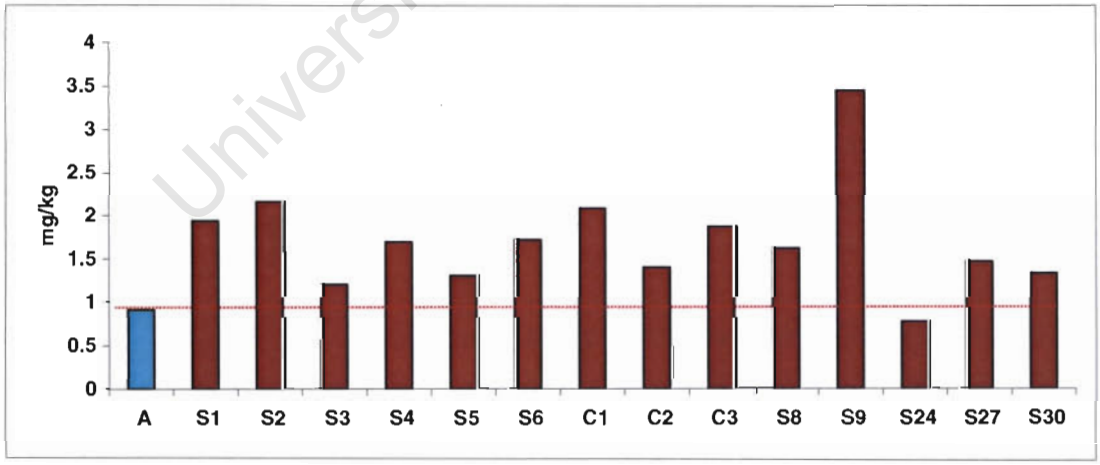

Figure 5.25 U (mg/kg) in Bulk soil samples

Arsenic

For arsenic the following samples are less than the background sample, S3, S5, S6, C2, S24 and S30. The samples above the concentration of the background samples are less than the average value of arsenic in soils, 6 mg/kg (Sparks, 1995).

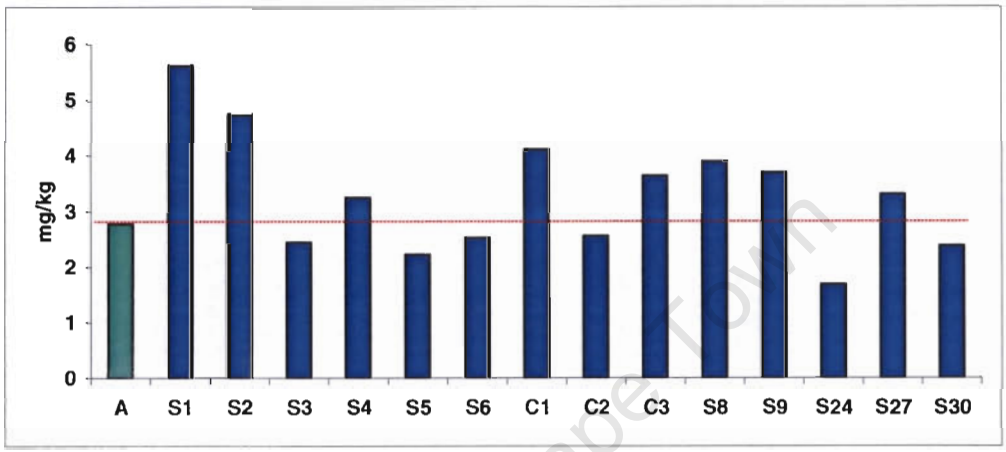

Figure 5.26 As (mg/kg) in Bulk soil samples

Selenium

For selenium only samples S3 and S9 shows elevated levels in relation to the background sample. The background sample however is higher than the average concentration listed by Sparks, (1995) of 0.4 mg/kg.

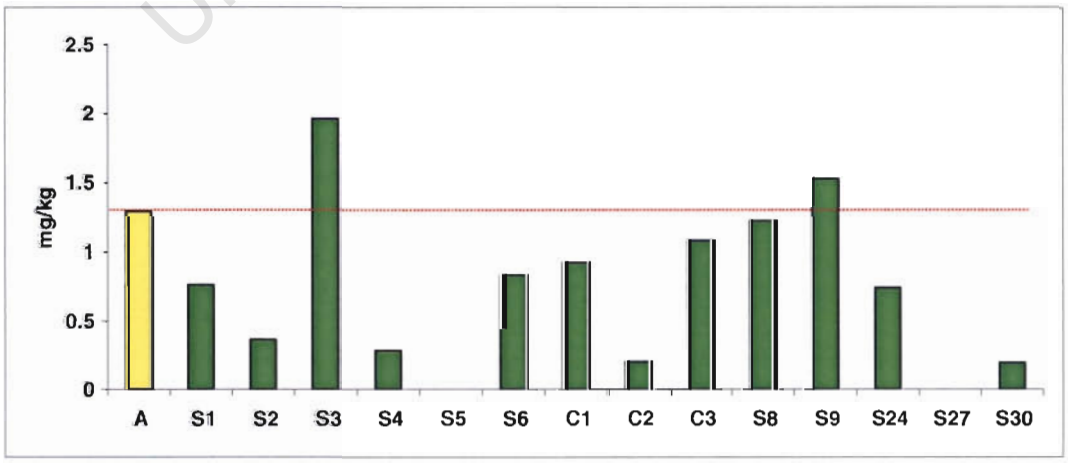

Figure 5.27 Se (mg/kg) in Bulk soil samples

CHAPTER 6

Conclusions

The main objective of this study was to investigate the effects of the disposal of sulphuric acid leach effluent in unlined evaporation ponds on the groundwater resources, and potential implications for contaminant migration in the subsurface environment.

The raw effluent entering the evaporation ponds shows elevated levels of contaminant in relation to the background waters sampled in the area. The effluent is also Na-SO_4 dominant whereas the natural environment is Na-Cl dominant, therefore the SO_4^{2-} ion was used as a useful tracer of the effluent movement.

The fact that all the evaporation ponds are unlined will cause some seepage around the ponds. However, the gypsum precipitate that formed in the ponds played an important role in retaining some of the contaminants. Although the neutralizing process seems not to be too effective, the acidic nature of the effluent is buffered as it finds its way to the seepage pond with an alkaline pH of 8.3. Major cations and anions increase in the cut-off trench except for SO_4 and K. Some of the trace elements are also accumulating in the cut-off trench. Uranium seems to accumulate in the cut-off trench and can be a reason for concern. The major cations and anions also increase towards the seepage pond except K that shows a decrease in concentration from the raw effluent. The only trace element that shows an increase was Se. The use of the cut-off trench water for irrigation purposes were ruled out due to its acidic nature and elevated levels of contaminants.

The soils sampled around the ponds to investigate the level of contaminants were mainly sandy loam soil. Only three of the soil samples reveal an acidic nature while the majority of the samples, including the background samples were moderately alkaline. The soils would therefore act as a good buffer for the acidic effluent seeping out of the evaporation ponds. The high base saturation observed is also quite normal for arid regions. The saturated paste extract results revealed that the soils could be classified as saline-sodic soils except for S2. These saline-sodic soils can be problematic for the usage of the soils for planting crops. Exchangeable Na will also affect the physical characteristics of the soil. SO_4^{2-} and Cl^- dominate the major cations and anions. The dominance of SO_4^{2-} is mainly from the effluent seeping from the ponds.

The trace element concentrations revealed elevated levels compared to the background samples. Elements of concern are Thorium and Uranium, because almost all the samples analysed were higher in concentration than the background samples. For Thorium, some of the samples exceed the world average value measured in soils. The same applies to Uranium also exceeding the world average value. For Arsenic and Selenium, only some of the samples exceed the background levels.

For all the boreholes, a neutral pH was observed except for G12. The waters were also found as highly saline water in the area. Oxidizing conditions also exist for all the boreholes. Chloride and sodium were found to be the dominant ions present in groundwater. Elevated levels in relation to the background boreholes exist for all the major anions and cations except for G8, Cl becomes less than the background samples. A strong marine influence exists in the background boreholes. Sulphate shows elevated levels in all the other water samples.

Trace elements of concern are Uranium, Arsenic, and Selenium, because they all exhibit elevated levels in relation to the background samples.

Based on the assessment of the water quality in terms of usage for irrigation, the level of contamination makes it unsuitable for this purpose.

From the spatial distribution maps, the contaminant plume seems to spread in a south-easterly direction towards G12 and G5.

CHAPTER 7

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Appendix A

Method Appraisal

4.2.1.1 pH measurements

Table A1: Results of pH readings for groundwater samples

Sample	pH Reading A	pH Reading B	Mean	SD	% RSD
G1 (Field)	7.2	7.2	7.2	0	0
G1 (Lab)	7.4	7.4	7.4	0	0
G4 (Field)	7.3	7.3	7.3	0	0
G4 (Lab)	7.6	7.6	7.6	0	0
G5 (Field)	6.7	6.7	6.7	0	0
G5 (Lab)	6.9	6.9	6.9	0	0
G7 (Field)	7.1	7.1	7.1	0	0
G7 (Lab)	7.4	7.4	7.4	0	0
G8 (Field)	7.2	7.2	7.2	0	0
G8 (Lab)	7.4	7.3	7.4	0.07	1.0
G9 (Field)	7.03	7.03	7.0	0	0
G9 (Lab)	7.6	7.5	7.6	0.07	0.9
G10 (Field)	6.8	6.8	6.8	0	0
G10 (Lab)	7.4	7.3	7.4	0.07	1.0
G11 (Field)	6.8	6.8	6.8	0	0
G11 (Lab)	7.3	7.2	7.3	0.07	1.0
G12 (Field)	5.1	5.1	5.1	0	0
G12 (Lab)	5.4	5.4	5.4	0	0

4.2.1.2 Electrical conductivity (EC)

Table A2: Results of EC readings for groundwater samples

Sample	EC Reading A	EC Reading B	Mean	SD	% RSD
G1 (Field)	27.2	27.1	27.2	0.07	0.3
G1 (Lab)	26.8	26.9	26.9	0.07	0.3
G4 (Field)	10.58	10.56	10.57	0.01	0.1
G4 (Lab)	10.42	10.39	10.41	0.02	0.2
G5 (Field)	50.2	50.4	50.3	0.003	0.01
G5 (Lab)	49.5	49.4	49.45	0.07	0.1
G7 (Field)	37.0	38.0	37.5	0.71	1.9
G7 (Lab)	35.0	35.0	35.0	0	0
G8 (Field)	9.20	9.26	9.23	0.04	0.5
G8 (Lab)	9.06	9.06	9.06	0	0
G9 (Field)	8.41	8.42	8.42	0.01	0.1
G9 (Lab)	8.32	8.32	8.32	0	0
G10 (Field)	7.93	7.92	7.93	0.01	0.1
G10 (Lab)	7.79	7.77	7.78	0.01	0.2
G11 (Field)	8.42	8.41	8.42	0.01	0.1
G11 (Lab)	8.36	8.37	8.37	0.01	0.1
G12 (Field)	27.0	27.0	27.0	0	0
G12 (Lab)	26.7	26.6	26.65	0.07	0.3

4.2.1.3 Eh and temperature measurements

Table A3: Eh measurements

Sample	Temperature °C	Eh (mV) Reading 1	Eh (mV) Reading 2	Mean	SD	% RSD	pe
G1	22.3	182	182	182	0	0	6.74
G4	21.9	167	161	164	4.2	2.6	6.38
G5	21.7	86	81	83.5	3.5	4.2	5.02
G7	22.7	179	167	173	8.5	4.9	6.48
G8	22.5	167	158	163	6.4	3.9	6.33
G9	22.3	127	157	142	21.2	14.9	6.31
G10	22.2	195	192	194	2.1	1.1	6.91
G11	22.8	205	206	205.5	0.7	0.3	7.13
G12	22.1	259	263	261	2.8	1.1	8.12

4.2.1.4 Alkalinity

Table A4: Results of alkalinity

Sample	Alkalinity (meq/L HCO_3^-) A	Alkalinity (meq/L HCO_3^-) B	Mean	SD	% RSD
G1	3.79	3.78	3.79	0.01	0.2
G4	4.10	4.14	4.12	0.03	0.7
G5	4.28	4.20	4.24	0.06	1.3
G7	3.13	3.09	3.11	0.03	0.9
G8	3.20	3.29	3.25	0.06	2.0
G9	3.55	3.57	3.56	0.01	0.4
G10	2.89	3.11	3.00	0.16	5.2
G11	2.45	2.38	2.42	0.05	2.1
G12	1.31	1.32	1.32	0.01	0.5

4.2.1.4 Table A5:Major ion chemistry of groundwater samples

Conc. (mg/L)	Na^+	Ca^{2+}	K^+	Mg^{2+}	F^-	Cl^-	SO_4^{2-}	PO_4^{3-}
G1 A	2591	587	188	626	2.27	4003	1443	2.8
G1 B	1339	582	182	624	2.23	3659	1325	2.8
Mean	**1965**	**585**	**185**	**625**	**2.25**	**3831**	**1384**	**2.8**
SD	885	3.5	4.2	1.4	0.03	243	83.4	0
%RSD	45.0	0.6	2.3	0.2	1.3	6.3	6.0	0
G4 A	1812	186	51	166	1.98	2917	490	5.6
G4 B	1780	197	52	177	1.99	2829	481	5.6
Mean	**1796**	**192**	**52**	**172**	**1.99**	**2873**	**486**	**5.6**
SD	22.6	7.8	0.7	7.8	0.01	62.2	6.4	0
%RSD	1.3	4.1	1.4	4.5	0.4	2.2	1.3	0
G5 A	10640	829	208	1411	0.64	12736	7421	27.2
G5 B	10651	829	207	1414	0.68	12055	7204	28.0
Mean	**10646**	**829**	**208**	**1413**	**0.66**	**12396**	**7313**	**27.6**
SD	7.8	0	0.7	2.1	0.03	481.5	153.4	0.6
%RSD	0.1	0	0.3	0.2	4.3	3.9	2.1	2.1
G7 A	6714	694	161	900	2.98	9570	2228	4.4
G7 B	6682	698	160	899	2.95	9570	2228	4.4
Mean	**6698**	**696**	**161**	**900**	**2.97**	**9570**	**2228**	**4.4**
SD	22.6	2.8	0.7	0.7	0.02	0	0	0
%RSD	0.3	0.4	0.4	0.1	0.7	0	0	0
G8 A	1264	256	95	327	3.10	1052	2025	6.0
G8 B	1209	262	97	337	3.07	968	2591	6.0
Mean	**1237**	**259**	**96**	**332**	**3.09**	**1010**	**2308**	**6.0**
SD	38.9	4.2	1.4	7.1	0.02	59.4	400.2	0
%RSD	3.2	1.6	1.5	2.1	0.7	5.9	17.3	0
G9 A	1426	149	58	143	2.57	2311	828	4.8
G9 B	1432	151	59	147	2.58	2331	828	5.2
Mean	**1429**	**150**	**59**	**145**	**2.58**	**2321**	**828**	**5.0**
SD	4.2	1.4	0.7	2.8	0.01	14.1	0	0.3
%RSD	0.3	0.9	1.2	2.0	0.3	0.6	0	5.7
G10 A	1288	143	54	143	1.64	2222	425	6.4
G10 B	1289	143	55	143	1.69	2213	418	6.8
Mean	**1289**	**143**	**55**	**143**	**1.67**	**2218**	**422**	**6.6**
SD	0.7	0	0.7	0	0.04	6.4	4.9	0.3
%RSD	0.1	0	1.3	0	2.1	0.3	1.2	4.3
G11 A	1423	150	49	151	1.70	2356	414	5.6
G11 B	1466	151	49	151	1.70	2317	415	6.0
Mean	**1445**	**151**	**49**	**151**	**1.70**	**2337**	**415**	**5.8**
SD	30.4	0.7	0	0	0	27.6	0.7	0.3
%RSD	2.1	0.5	0	0	0	1.2	0.2	4.9
G12 A	5333	420	134	585	1.31	7086	2555	4.0
G12 B	5321	414	132	576	1.21	7086	2534	4.0
Mean	**5327**	**417**	**133**	**581**	**1.26**	**7086**	**2545**	**4.0**
SD	8.5	4.2	1.4	6.4	0.1	0	14.9	0
%RSD	0.2	1.0	1.1	1.1	5.6	0	0.6	0

4.2.1.5 Silica

Table A6: Silica measurements

Sample	SiO_2 conc. A (mg/L)	SiO_2 conc. B (mg/L)	Mean	SD	% RSD
G1	23.85	21.95	22.90	1.3	5.9
G4	11.92	11.92	11.92	0	0
G5	20.80	22.90	21.85	1.5	6.8
G7	9.34	9.92	9.63	0.4	4.3
G8	21.75	22.33	22.04	0.4	1.9
G9	17.71	18.05	17.88	0.2	1.3
G10	24.24	22.14	23.19	1.5	6.4
G11	22.90	22.52	22.71	0.3	1.2
G12	11.65	12.36	12.01	0.5	4.2

The results presented in Table A7 give the published values for the NIST-1640 standard, the UCT measured concentration, the standard deviation and the percentage error between the two values.

Table A7: ICP-MS Analysis of NIST Water: NIST 1640 All data in ppb

Element	NIST-1640	UCT	RSD	% Error
Li	50.0	50.7	1.0	-1.4
Be	34.8	34.94	0.3	0.4
B	278	301.1	5.6	7.6
Na	28088	29350	3.1	4.3
Mg	5026	5819	10.3	13.6
Al	62.2	52.0	12.6	-19.6
Si	3517	4730	20.8	26.7
K	1050	994	3.9	-5.6
Ca	6379	7045	7.0	9.5
Ti	7.34	-		
V	11.7	12.99	7.4	9.9
Cr	37.3	38.6	2.4	3.4
Mn	120	121.5	0.9	1.2
Fe	31.2	34.3	6.7	9.0
Co	20.0	20.28	1.0	1.4
Ni	28.2	27.4	2.0	-2.9
Cu	93.7	85.2	6.7	-9.9
Zn	75.3	53.2	24.3	-41.5
As	25.8	26.67	2.3	3.3
Se	22.1	21.96	0.5	-0.6
Rb	2.00	2.00	0	0
Sr	122	124.2	1.3	1.8
Zr	0.37	-		
Mo	46.6	46.75	0.2	0.3
Ag	7.03	7.62	5.7	7.7
Cd	22.9	22.79	0.3	-0.5
Ba	146	148.0	1.0	1.4
Pb	30.0	27.89	5.2	-7.6
Th	0.11	-		
U	0.78	-		

4.2.1.6 Table A8: ICP-MS analysis

Conc. (mg/L)	Fe	B	Si	Sr	Ti
G1 A	1.34	6.94	14.71	4.20	1.14
G1 B	1.29	6.94	14.21	4.18	1.14
Mean	**1.31**	**6.94**	**14.46**	**4.19**	**1.14**
SD	0.04	0	0.4	0.01	0
%RSD	2.7	0	2.5	0.3	0
G4 A	0.43	2.42	7.44	1.67	0.35
G4 B	0.44	2.35	7.40	1.66	0.35
Mean	**0.43**	**2.38**	**7.42**	**1.66**	**0.35**
SD	0.01	0.1	0.03	0.01	0
%RSD	1.6	2.1	0.4	0.4	0
G5 A	2.27	9.44	16.51	8.45	1.72
G5 B	2.27	9.44	16.51	8.45	1.72
Mean	**2.27**	**9.44**	**16.51**	**8.45**	**1.72**
SD	0	0	0	0	0
%RSD	0	0	0	0	0
G7 A	1.65	4.66	5.19	6.00	1.06
G7 B	1.63	4.62	5.30	5.99	1.10
Mean	**1.64**	**4.64**	**5.24**	**5.99**	**1.08**
SD	0.01	0.03	0.1	0.01	0.03
%RSD	0.9	0.6	1.5	0.1	2.6
G8 A	0.70	6.80	14.21	1.99	0.69
G8 B	0.63	7.22	13.66	1.91	0.65
Mean	**0.67**	**7.01**	**13.94**	**1.95**	**0.67**
SD	0.05	0.3	0.4	0.1	0.03
%RSD	7.4	4.2	2.8	2.9	4.2
G9 A	0.23	1.95	1.13	0.93	0.27
G9 B	0.29	2.05	1.14	0.93	0.26
Mean	**0.26**	**2.00**	**1.14**	**0.93**	**0.26**
SD	0.04	0.1	0.01	0	0.01
%RSD	16.3	3.5	0.6	0	2.7
G10 A	0.33	1.62	15.00	1.09	0.29
G10 B	0.31	1.78	15.00	1.08	0.26
Mean	**0.32**	**1.70**	**15.00**	**1.08**	**0.27**
SD	0.01	0.1	0	0.01	0.02
%RSD	4.4	6.7	0	0.7	7.7
G11 A	0.38	1.76	15.26	1.09	0.30
G11 B	0.29	1.83	14.72	1.07	0.28
Mean	**0.33**	**1.79**	**14.99**	**1.08**	**0.29**
SD	0.1	0.1	0.4	0.01	0.01
%RSD	18.9	2.8	2.5	1.3	4.9
G12 A	1.18	5.82	7.11	4.74	0.97
G12 B	1.08	5.22	6.97	4.69	1.02
Mean	**1.13**	**5.52**	**7.04**	**4.71**	**0.99**
SD	0.1	0.4	0.1	0.04	0.04
%RSD	6.3	7.7	1.4	0.8	3.6

Table A8: ICP-MS analysis (cont)

Conc. (µg/L)	Ni	Zn	Zr	Al	Th	U	Li	Co	Cu	As	Se	Cd	Ba	Mn
G1 A	14.2	95.6	1.03	14.0	0.02	29.4	4.88	0.70	29.8	54.6	108	0.10	40.1	1.69
G1 B	14.2	96.2	1.46	8.22	0.01	28.9	4.55	0.60	31.7	55.0	98.5	0.09	40.3	1.96
Mean	**14.2**	**95.9**	**1.24**	**11.1**	**0.01**	**29.13**	**4.7**	**0.65**	**30.8**	**54.8**	**103.2**	**0.1**	**40.2**	**1.8**
SD	0	0.4	0.3	4.1	0.01	0.4	0.2	0.1	1.3	0.3	6.7	0.01	0.1	0.2
%RSD	0	0.4	24.4	36.8	47.1	1.2	4.9	10.9	4.4	0.5	6.5	7.4	0.4	10.5
G4 A	10.3	33.6	0.61	8.92	n.d	0.61	36.8	0.52	17.6	21.2	33.7	0.85	28.8	8.08
G4 B	10.2	35.3	0.56	9.29	n.d	0.61	38.0	0.41	17.5	21.1	35.4	0.68	27.9	8.64
Mean	**10.3**	**34.43**	**0.58**	**9.10**	n.d	**0.61**	**37.4**	**0.46**	**17.5**	**21.1**	**34.6**	**0.8**	**28.4**	**8.4**
SD	0.1	1.2	0.04	0.3		0	0.9	0.1	0.1	0.1	1.2	0.1	0.6	0.4
%RSD	0.7	3.5	6.0	2.9		0	2.3	16.7	0.4	0.3	3.5	15.7	2.2	4.7
G5 A	64.2	278	1.87	20.3	0.04	21.9	103	16.4	83.4	87.4	177	1.14	79.8	6773
G5 B	64.2	278	1.87	20.3	0.04	21.9	103	16.4	83.4	87.4	177	1.14	79.8	6773
Mean	**64.2**	**278**	**1.87**	**20.3**	**0.04**	**21.9**	**103**	**16.4**	**83.4**	**87.4**	**177**	**1.1**	**79.8**	**6773**
SD	0	0	0	0	0	0	0	0	0	0	0	0	0	0
%RSD	0	0	0	0	0	0	0	0	0	0	0	0	0	0
G7 A	17.7	142	2.97	7.80	0.02	27.3	20.6	1.17	37.1	75.1	178	0.24	26.6	2.19
G7 B	17.5	147	2.14	6.48	0.02	27.0	21.1	1.00	39.7	74.1	173	0.24	26.6	2.33
Mean	**17.6**	**144**	**2.55**	**7.14**	**0.02**	**27.15**	**20.8**	**1.08**	**38.4**	**74.6**	**176**	**0.2**	**26.6**	**2.3**
SD	0.1	3.5	0.6	0.9	0	0.2	0.4	0.1	1.8	0.7	3.5	0	0	0.1
%RSD	0.8	2.4	22.9	13.1	0	0.8	0.03	11.1	4.8	0.9	2.0	0	0	4.4
G8 A	10.1	129	1.62	8.17	0.04	10.1	8.15	0.56	19.2	7.47	38.3	0.67	12.2	3.89
G8 B	7.88	125	1.34	7.96	0.03	9.84	7.94	0.43	9.74	4.33	37.1	0.82	12.4	3.53
Mean	**8.99**	**127**	**1.48**	**8.06**	**0.03**	**9.97**	**8.0**	**0.49**	**14.5**	**5.9**	**37.7**	**0.7**	**12.3**	**3.7**
SD	1.6	2.8	0.2	0.2	0.01	0.2	0.2	0.1	6.7	2.2	0.9	0.1	0.1	0.3
%RSD	17.5	2.2	13.4	1.8	20.2	1.8	1.9	18.6	46.2	37.6	2.3	14.2	1.2	6.9
G9 A	4.87	38.3	0.38	7.10	0.05	5.55	6.22	0.45	8.62	16.3	41.8	0.59	34.8	10.8
G9 B	4.77	36.8	0.74	7.57	n.d	5.50	6.69	0.42	7.67	20.8	32.8	0.89	33.6	9.43
Mean	**4.82**	**37.5**	**0.56**	**7.34**	**0.05**	**5.52**	**6.5**	**0.44**	**8.1**	**18.5**	**37.34**	**0.7**	**34.2**	**10.1**
SD	0.1	1.1	0.3	0.3		0.04	0.3	0.02	0.7	3.2	6.4	0.2	0.9	1.0
%RSD	1.5	2.8	45.5	4.5		0.6	5.2	4.9	8.2	17.2	1.1	28.7	2.5	9.6
G10 A	4.75	27.1	1.19	5.16	0.01	2.55	8.04	0.20	8.35	16.7	32.4	0.69	44.5	2.40
G10 B	4.59	26.1	0.60	3.06	n.d	2.56	7.88	0.29	7.32	16.0	34.3	0.64	43.6	2.06
Mean	**4.67**	**26.6**	**0.90**	**4.11**	**0.01**	**2.55**	**8.0**	**0.24**	**7.8**	**16.4**	**33.35**	**0.7**	**44.1**	**2.2**
SD	0.1	0.7	0.4	1.5		0.01	0.1	0.1	0.7	0.5	1.3	0.04	0.6	0.2
%RSD	2.4	2.7	46.6	36.1		0.3	1.4	25.9	9.3	3.0	4.0	5.3	1.4	10.8
G11 A	6.54	43.1	0.80	10.9	n.d	2.69	11.2	1.02	14.5	20.3	41.8	0.95	41.0	4.80
G11 B	5.29	43.7	1.75	8.19	0.01	2.73	10.2	0.93	9.56	19.3	38.9	0.86	40.4	4.43
Mean	**5.91**	**43.4**	**1.27**	**9.56**	**0.01**	**2.71**	**10.7**	**0.98**	**12.0**	**19.97**	**40.4**	**0.9**	**40.7**	**4.6**
SD	0.9	0.4	0.7	1.9		0.03	0.7	0.1	3.5	0.7	2.1	0.1	0.4	0.3
%RSD	14.9	1.0	52.7	20.1		1.0	6.6	6.5	29.0	3.6	5.1	7.0	1.0	5.7
G12 A	333	331	1.14	1210	0.02	34.0	247	244	63.9	49.1	144	12.2	32.5	674
G12 B	335	376	1.85	1266	0.01	34.2	239	246	67.8	44.8	150	12.2	34.4	669
Mean	**334**	**354**	**1.49**	**1238**	**0.02**	**34.10**	**243**	**245**	**65.9**	**46.93**	**147**	**12.2**	**33.4**	**672**
SD	1.4	31.8	0.5	39.6	0.01	0.1	5.7	1.4	2.8	3.0	4.2	0	1.3	3.5
%RSD	0.4	9.0	33.6	3.2	47.1	0.4	2.3	0.6	4.2	6.5	2.9	0	4.0	0.5

Appendix B: Results

	A	B	C	S1	S2	S3	S4	S5	S6	C1	C2	C3	S8	S9
GPS S	31.46206	31.46206	31.46206	31.46814	31.46790	31.46773	31.46759	31.46731	31.46716	31.46840	31.46921	31.46950	31.46986	31.46680
E	18.29764	18.29764	18.29764	18.29622	18.29647	18.29697	18.29720	18.29761	18.29782	18.29596	18.29988	18.29998	18.30032	18.29936
pH (H_2O)	8.5	8.0	8.3	8.9	6.4	8.8	9.5	9.0	9.0	7.1	8.4	8.0	9.0	4.8
pH (KCl)	7.9	7.1	7.8	8.1	5.7	8.4	8.1	8.5	8.4	6.5	7.8	7.5	8.5	4.2
1 M KCl extractable ($mmole_c$/kg soil)														
Acidity														
Ca^{2+}	2.45	2.42	2.28	2.86	40.00	3.27	3.72	9.71	16.69	29.77	9.35	11.41	15.65	16.89
Mg^{2+}	2.38	5.98	5.77	3.62	13.10	2.65	0.94	1.88	1.53	18.86	9.82	17.98	3.65	2.63
Particle Size distribution (%)														
Coarse sand	9.4	8.1	16.9	10.3	31.4	7.7	15.6	18.4	11.5	11.2	5.8	5.0	21.1	16.3
Sand Fraction	72.8	67.5	64.3	68.7	49.6	71.9	65.2	62.6	67.5	72.6	69.4	56.2	59.1	60.5
Silt Fraction	7.6	6.6	5.2	6.0	5.8	7.6	7.6	6.8	6.2	4.4	9.4	19.6	8.2	7.8
Clay Fraction	10.2	17.8	13.6	15.0	13.2	12.8	11.6	12.2	14.8	11.8	15.4	19.2	11.6	15.4
% Organic C	0.16	0.04	0.0	0.08	0.27	0.27	0.03	0.12	0.14	0.18	0.50	0.79	0.06	0.90
Paste Extract														
pH	7.7	6.9	7.3	7.9	5.9	7.5	8.5	7.7	8.2	5.5	7.3	7.1	8.2	5.0
EC (mS/cm)	39.2	77.0	54.7	16.78	64.5	59.7	8.91	72.5	27.5	166.7	139.7	165.4	50.9	10.11
Major ions														
Na^+	1289	2978	2056	513	1589	1550	219.9	1970	762	1626	1134	6381		134.0
Mg^{2+}	900	2940	1935	353.5	5547	1223	55.1	897	374.3	8896	7576	9258		603
Ca^{2+}	1247	1767	1223	479.5	2253	1726	360.0	1741	878	1351	859	1008		614
K^+	261.1	473.9	320.8	169.6	176.1	434.0	96.0	235.1	155.2	777	1067	981		157.3
F^-														
Br	-	-	-	-	-	-	3.90	-	-	-		-	-	4.0
NO_3^-	188.25	182.00	217.50	33.13	317.00	416.50	22.50	149.50	32.00	416.25		467.50	120.50	27.70
Cl^-	13039.00	27939.00	20571.00	736.25	23388.50	21374.50	997.60	24112.00	5950.88	84641.25		75025.00	11583.00	1248.60
SO_4^{2-}	1621.00	5688.00	3690.00	275.50	4544.00	2011.00	3275.10	4747.00	5393.50	11313.75		17712.50	18257.50	4787.30
PO_4	124.50	236.00	234.00	59.13	237.00	235.50	47.60	233.00	-	-		585.00	256.00	46.80

	A	B	C	S1	S2	S3	S4	S5	S6	C1	C2	C3	S8	S9
Conc. mg/L														
B	5.46	27.80	23.25	14.38	3.31	4.19	11.81	15.87	47.52	51.94	24.22	8.97	62.33	9.54
Al	0.01	0.03	0.02	0.03	0.04	0.03	0.03	0.05	0.04	0.05	0.07	0.06	0.04	5.63
Si	26.53	33.25	12.56	7.55	27.44	9.90	16.34	10.15	11.89	98.01	26.86	22.78	8.65	58.79
Ti	2.55	5.00	2.85	0.96	4.92	3.17	0.90	4.49	2.62	5.52	5.53	4.26	4.03	1.37
V	0.04	0.17	0.11	0.08	0.12	0.21	n.d	0.29	0.02	0.70	0.46	0.49	0.04	0.03
Mn	0.10	0.74	0.83	0.02	12.15	0.09	0.02	0.03	0.06	8.55	0.17	0.11	0.02	49.30
Fe	4.08	5.84	3.94	1.24	6.72	4.43	0.97	5.09	3.17	4.96	3.69	3.15	2.65	1.50
Sr	13.86	23.74	17.14	6.38	16.91	23.45	2.06	39.84	18.65	45.46	15.37	15.36	11.33	4.40
Conc. µg/L														
Th	0.03	0.17	0.05	0.15	0.79	0.20	0.02	0.29	0.02	0.44	0.46	0.75	0.08	0.35
U	0.85	0.13	2.38	3.04	0.58	3.45	11.7	10.6	12.6	0.19	6.68	3.91	45.2	1.77
Li	68.8	177	90.3	63.0	55.8	182	37.0	172	270	553	299	268	159	477
Zn	80.5	239	176	87.2	344	153	118	247	208	525	721	711	431	436
Pb	2.62	3.04	2.94	2.80	6..05	2.83	0.39	2.83	1.91	16.8	5.49	6.12	2.41	6.82
Zr	1.22	1.39	1.54	1.05	7.72	1.67	0.85	2.48	2.13	1.73	3.86	3.17	1.88	1.09
Cr	6.36	26.3	14.8	22.1	19.2	17.8	19.2	29.1	19.4	50.1	44.7	37.1	19.1	12.4
Ni	41.7	76.7	49.0	17.3	110.7	48.5	20.1	58.2	39.2	107	77.3	84.6	43.4	637
Rb	35.2	42.6	31.4	16.1	23.2	58.4	11.0	37.1	22.4	122	168	162	36.1	37.9
Be	n.d	5.26	n.d	2.74	n.d	1.38	n.d	13.2	n.d	45.3	35.4	39.5	3.75	4.20
Co	3.27	11.4	8.79	3.15	27.0	8.72	3.10	6.90	8.29	50.7	12.7	14.4	4.74	199
Cu	93.3	181	112	61.7	283	191	48.7	293	129	677	636	668	185	52.4
As	85.7	197	134	40.4	194	162	8.73	214	50.7	672	466	645	85.6	7.36
Se	217	447	332	76.1	260	161	17.8	35.8	46.6	354	653	764	137	26.3
Mo	5.19	57.5	130	23.4	1.06	2.50	71.0	64.6	10.1	7.47	20.1	4.59	75.4	0.76
Ag	0.51	4.48	0.20	2.76	1.14	2.44	0.14	2.87	0.013	18.6	1.29	8.97	n.d	0.82
Cd	1.69	0.97	0.95	0.48	18.1	1.50	0.33	1.10	0.49	4.85	16.6	35.9	0.48	6.22
Ba	62.4	122	74.2	153	407	393	58.0	141	94.0	169	228	143	134	107

	A	B	C	S1	S2	S3	S4	S5	S6	C1	C2	C3	S8	S9
Conc. mg/L														
Na	5879	8077	8650	9857	11163	12398	11949	14340	11982	19936	15683	22267	9884	6466
K	12103	17055	12576	26678	23245	24249	27922	35177	25291	27392	21593	24488	19246	17683
Mg	3735	7327	8724	10551	5904	5633	5393	3755	6462	7987	3909	8038	6752	5328
Ca	1742	2086	2852	3365	17373	3878	5523	5174	7096	9619	4030	7036	8705	6013
B	22.7	55.7	37.8	62.6	34.6	27.1	40.7	30.7	47.0	60.0	16.8	29.2	45.8	27.6
Al	36672	56055	47155	64456	66043	51357	65265	61352	59311	66818	55279	76061	55443	49305
Si	135.03	284.18	260.49	648.39	566.28	282.40	355.12	360.73	401.55	852.16	283.78	638.84	294.53	211.38
Ti	2127	2542	2024	3013	3222	2869	2634	2195	3103	2445	2166	3178	2158	2391
V	41.8	69.7	56.8	67.8	65.4	43.2	47.6	35.2	45.9	54.9	41.2	63.1	47.9	55.1
Mn	356	199	182	580	245	618	392	330	738	207	347	724	361	278
Fe	19171	25722	22386	27164	29222	18032	22106	15329	21012	26323	18235	25309	26647	22789
Sr	73.4	91.9	78.7	99.1	132	76.9	85.5	93.2	126	91.3	85.7	159	227	79.8
Th	7.00	12.5	14.6	15.3	13.8	8.83	11.4	7.29	11.8	10.8	8.62	12.7	8.53	19.2
U	0.91	2.11	1.98	1.93	2.15	1.20	1.69	1.30	1.71	2.07	1.39	1.86	1.61	3.45
Li	17.9	23.1	17.1	29.0	20.6	17.8	20.7	15.5	21.3	27.1	18.7	29.9	22.5	22.8
Zn	64.5	80.0	60.8	115	110	80.5	82.9	56.4	92.0	55.7	50.7	76.5	70.0	75.3
Pb	12.5	15.2	12.1	24.0	22.2	19.9	22.2	22.7	21.8	13.0	18.6	16.6	20.5	17.3
Zr	34.6	43.2	31.8	44.8	54.8	32.7	39.0	28.3	37.3	34.2	23.1	34.4	30.1	33.6
Cr	39.5	59.3	49.4	56.3	60.9	36.2	40.8	31.3	38.4	49.9	33.5	49.8	41.6	66.5
Ni	10.9	19.8	16.6	17.9	15.6	11.1	12.9	8.81	12.7	13.9	8.76	15.1	14.9	13.6
Co	5.69	6.89	5.60	10.1	6.18	5.91	6.64	5.37	7.56	4.92	4.15	6.47	6.51	5.50
Cu	17.5	38.3	43.9	26.3	25.9	14.4	21.8	14.2	17.4	18.1	14.2	21.3	22.3	22.3
As	2.77	6.53	6.28	5.62	4.74	2.44	3.24	2.22	2.52	4.10	2.55	3.63	3.88	3.69
Se	1.29	n.d	n.d	0.76	0.36	1.96	0.28	n.d	0.83	0.92	0.20	1.08	1.22	1.53
Mo	0.49	0.72	0.72	0.96	1.21	0.52	0.72	0.59	0.64	0.77	0.57	0.71	0.60	0.67
Ag	0.20	0.22	0.14	0.25	0.33	0.23	0.24	0.17	0.23	0.25	0.19	0.28	0.17	0.23
Cd	0.085	0.057	0.017	0.13	0.043	0.091	0.092	0.050	0.090	0.023	0.054	0.048	0.063	0.053
Rb	63.2	82.2	58.7	147	139	126	151	171	133	155	124	131	106	96.4
Ba	401	291	257	509	447	519	527	666	524	468	512	489	461	403

	Pore A	Pore B	S17	S18	S19	S20	S24	S25	S26	S27	S28	S29	S30	S31
GPS S	31.46840	31.46840					31.46983	31.46983	31.46983	31.46734	31.46734	31.46734	31.46977	
E	18.29596	18.29596					18.29510	18.29510	18.29510	18.29908	18.29908	18.29908	18.30023	
pH (H_2O)	9.0	8.4	9.6	8.4	8.5	8.4	7.5	7.6	7.7	7.9	6.6	5.5	8.0	7.9
pH (KCl)	8.4	7.6	8.2	7.6	7.9	7.8	7.1	6.5	6.7	7.4	6.0	4.7	7.5	7.0
1 M KCl extractable ($mmole_c$/kg soil)														
Acidity														
Ca^{2+}	9.41	1.91	3.67	1.89	2.65	8.91	4.12	0.84	1.06	6.50	1.27	2.00	3.42	2.86
Mg^{2+}	13.05	3.10	0.89	3.16	2.48	11.08	2.66	1.35	1.75	18.67	8.89	8.25	3.38	6.03
Particle Size distribution (%)														
Coarse sand	8.1	14.6	18.0	16.5	8.1	6.0	19.0	29.5	32.6	9.5	13.7	20.9	34.7	7.7
Sand Fraction	50.5	66.0	60.2	70.1	77.9	72.2	63.6	54.3	56.0	65.5	53.3	56.5	42.3	72.1
Silt Fraction	15.4	6.6	8.2	3.2	3.0	8.6	7.6	4.0	0.6	10.0	3.6	3.6	7.8	5.2
Clay Fraction	26.0	12.8	13.6	10.2	11.0	13.2	9.8	12.2	10.8	15.0	29.4	19.0	15.2	15.0
% Organic C	1.56	0.09	0.01	0.05	0.05	0.27	0.25	0.01	0.002	0.71	0.22	0.00	0.19	0.04
Paste Extract														
PH	7.9	7.8	8.3	7.9	7.7	7.4	7.7	7.3	7.2	6.8	7.7	5.3	7.8	7.2
EC (mS/cm)	80.7	53.8	8.55	57.0	42.3	121.9	23.8	30.6	42.1	219	79.3	67.3	68.1	55.0
Major ions														
Na^{+}	713	744	169.1	1417	533	1939	1643	6615	9407	85707	16279	14421	15885	11110
Mg^{2+}	2258	1601	52.9	1726	1013	6349	1114	644	1013	13789	4013	2328	2320	1750
Ca^{2+}	653	716	341.2	744	1355	823	2079	471.7	758	1347	785	673	1008	1089
K^{+}	885	477.3	97.9	524	277.0	903	199.76	177.64	222.20	183.02	291.02	245.37	318.57	373.51
F^{-}														
Br	-	-	1.6	-	-	-	-	-	-	-		-	-	-
NO_3^{-}	240	184	25.2	123.5	279.5	302								
Cl^{-}	16132	12717	896.4	13617.5	14741	47861								
SO_4^{2-}	24635	17335.5	3084.3	18243.5	1648.5	21724								
PO_4	-	239	46.7	235	-	482								

	Pore A	Pore B	S17	S18	S19	S20	S24	S25	S26	S27	S28	S29	S30	S31
Conc. mg/L														
B	20.31	6.50	9.62	8.41	4.12	9.16	0.22	6.36	7.78	2.82	2.51	5.81	5.13	15.17
Al	0.16	0.10	0.02	0.03	0.02	0.05	0.02	0.03	0.03	0.02	0.02	0.10	0.02	0.04
Si	12.28	20.71	13.60	22.48	21.75	17.63	13.11	26.71	19.77	1.29	13.43	28.42	11.29	11.43
Ti	5.96	3.24	0.74	3.49	2.63	4.86	2.99	1.20	1.71	2.70	1.65	1.34	2.14	2.13
V	0.09	0.12	n.d	0.14	0.03	0.33	0.01	0.03	0.04	0.54	0.12	0.08	0.10	0.10
Mn	1.05	2.42	0.02	6.46	0.12	0.12	1.81	0.20	0.31	2.18	1.35	3.10	23.97	0.43
Fe	2.83	2.03	1.04	2.22	4.36	2.64	8.48	1.59	2.83	4.94	2.65	2.14	3.03	4.02
Sr	22.17	15.30	2.00	16.75	15.28	13.12	12.35	4.61	7.83	47.18	13.42	12.07	9.36	15.76
Conc. µg/L														
Th	0.63	0.61	0.27	0.81	0.51	1.46	0.06	0.07	0.08	0.29	0.15	0.86	0.14	0.04
U	174	136	11.1	240	0.98	3.50	4.67	0.15	0.26	0.31	0.60	0.38	2.56	0.12
Li	193	108	31.7	120	73.9	187	40.8	42.4	96.8	784	130	168	134	153
Zn	676	541	107	575	75.1	785	47.3	185	293	520	203	228	339	221
Pb	3.04	3.76	0.77	5.02	3.56	22.7	2.12	3.01	4.67	24.4	9.82	12.2	3.87	4.50
Zr	3.91	2.59	0.67	2.86	1.14	3.93	2.66	1.38	4.00	5.12	4.30	4.86	2.79	2.51
Cr	29.8	22.4	10.1	27.6	7.58	31.4	5.01	2.87	7.65	20.8	14.2	8.76	10.2	17.3
Ni	268	118	17.1	133	46.8	66.9	84.1	21.9	51.5	103	53.2	50.2	83.6	43.1
Rb	165	82.2	10.1	90.4	37.2	129	29.7	29.3	35.9	331	32.7	29.3	44.9	34.4
Be	39.5	6.42	n.d	29.7	n.d	12.9	0.29	0.49	0.64	15.6	3.45	3.99	3.99	0.93
Co	67.1	19.6	2.71	35.8	3.02	10.0	7.94	4.63	4.01	28.5	11.5	16.0	37.3	7.24
Cu	298	303	31.8	253	92.3	536	25.0	47.9	83.7	790	164	137	156	98.9
As	250	112	6.33	127	84.1	378	63.6	58.6	75.0	792	178	132	130	143
Se	564	564	18.4	606	250	556	111	108	199	n.d	343	292	209	329
Mo	630	1065	67.1	1250	5.34	17.7	11.8	6.68	12.3	5.52	652	4.21	36.1	60.6
Ag	0.12	1.79	n.d	1.92	0.53	2210	0.76	0.6	0.69	20.4	1.70	1.76	1.14	1.38
Cd	1.58	2.94	0.35	3.40	1.96	11.6	2.01	0.97	2.44	140.9	13.6	9.07	11.8	1.43
Ba	117	101	51.2	119	67.6	189	801	101	96.0	224	25.0	61.9	185	53.2

	Pore A	Pore B	S17	S18	S19	S20	S24	S25	S26	S27	S28	S29	S30	S31
Conc. mg/L														
Na	22940	11491	11869	9330	5594	18389	4723	11633	10099	24224	14307	12035	11715	10062
K	22181	22882	25715	20332	11488	24662	14561	27452	19839	23137	25048	21447	22762	18029
Mg	7330	2546	5593	2194	3562	4161	1551	1115	872	7943	4581	6313	3390	6683
Ca	18558	1865	5728	1621	1765	4638	1168	1493	1281	3472	1694	1438	2293	2221
Al	51903	45014	62943	39564	34442	59356	29985	45518	34733	49482	60324	71160	49754	50089
Si	350.93	127.60	364.31	94.33	77.91	289.75	74.68	179.59	138.12	415.73	381.29	680.54	118.60	427.29
Ti	1905	1612	3002	1399	2332	2851	1609	2091	1698	2798	2307	2624	2212	2560
V	37.1	27.7	49.4	24.9	41.6	44.0	26.8	28.4	23.6	45.2	49.7	72.1	44.2	75.4
Mn	236	117	450	103	345	343	99.1	89.9	89.5	677	237	250	301	222
Fe	19950	11737	22975	10411	17641	18477	12243	12791	12885	19034	22725	35526	18823	24765
Sr	307	54.6	85.7	50.0	70.9	90.6	52.8	55.6	44.0	99.0	74.2	74.9	109	106
Th	9.39	7.47	9.62	4.39	5.38	9.55	5.94	9.08	5.18	11.0	11.0	15.71	8.68	11.3
U	3.64	1.57	1.64	1.19	0.84	1.68	0.77	1.47	1.39	1.46	1.59	2.30	1.32	2.31
Li	21.2	14.7	19.9	11.4	16.4	18.9	12.7	9.20	8.13	73.0	21.7	30.9	18.8	23.5
Be	-	-	-	-	-	-	1.16	1.78	1.38	1.68	1.96	1.96	2.06	1.77
B	56.4	21.1	32.7	17.6	19.6	20.5	1.15	4.47	n.d	14.1	19.7	24.5	14.1	45.4
Zn	39.2	41.6	96.5	64.8	73.5	67.3	39.3	43.6	36.3	69.7	84.8	112	68.9	97.4
Pb	10.4	18.5	22.2	15.8	11.5	20.5	14.5	27.9	16.8	11.5	22.3	19.6	19.9	15.6
Zr	27.4	17.0	41.8	27.0	39.6	30.3	14.9	23.2	14.0	37.8	40.5	57.7	35.0	45.4
Cr	37.5	25.1	44.6	23.3	39.9	37.6	21.8	26.0	20.9	40.4	46.2	69.6	37.6	65.7
Ni	12.4	7.72	13.6	6.72	10.4	8.81	5.41	4.72	4.26	12.9	12.1	18.5	11.1	22.2
Co	6.41	3.33	7.05	2.81	5.42	4.17	2.06	2.30	1.92	6.02	5.22	6.58	5.57	7.56
Cu	14.5	10.3	20.1	8.71	21.0	15.5	10.5	9.74	7.02	14.8	17.0	25.3	16.0	44.1
As	1.87	1.96	3.55	1.80	2.69	2.51	1.68	2.05	1.42	3.30	3.56	4.99	2.37	7.10
Se	0.26	0.86	0.83	0.65	2.70	0.62	0.74	n.d	n.d	n.d	0.08	1.27	0.19	0.67
Mo	1.50	0.96	0.80	0.88	0.48	0.59	0.42	0.50	0.38	0.66	0.78	1.10	0.52	0.80
Ag	0.17	0.12	0.28	0.22	0.23	0.26	0.19	0.17	0.11	0.26	0.25	0.27	0.23	0.25
Cd	0.02	0.04	0.11	0.03	0.08	0.09	0.05	0.10	0.03	0.03	0.11	0.04	0.05	0.03
Rb	117	120	138	108	60.7	130	78.1	145	105	123	141	136	120	88.8
Ba	468	549	526	516	439	531	364	550	529	502	507	369	476	319

Appendix C: Derived results

B. 1 sodium adsorption ratio (SAR)

The sodium adsorption ratio of the soil solution was calculated using the concentrations of Na^+, Ca^{2+} and Mg^{2+} obtained from AA analysis, according to the following equation (McBride, 1994):

$$SAR = [Na^+] / \{\sqrt{([Mg^{2+}] + [Ca^{2+}])/2}\}$$

B.2 Effective cation exchange capacity

Effective cation exchange capacity (ECEC) was calculated using the KCl extractable acidity, and Ca^{2+} and Mg^{2+} concentrations according to the following equation.

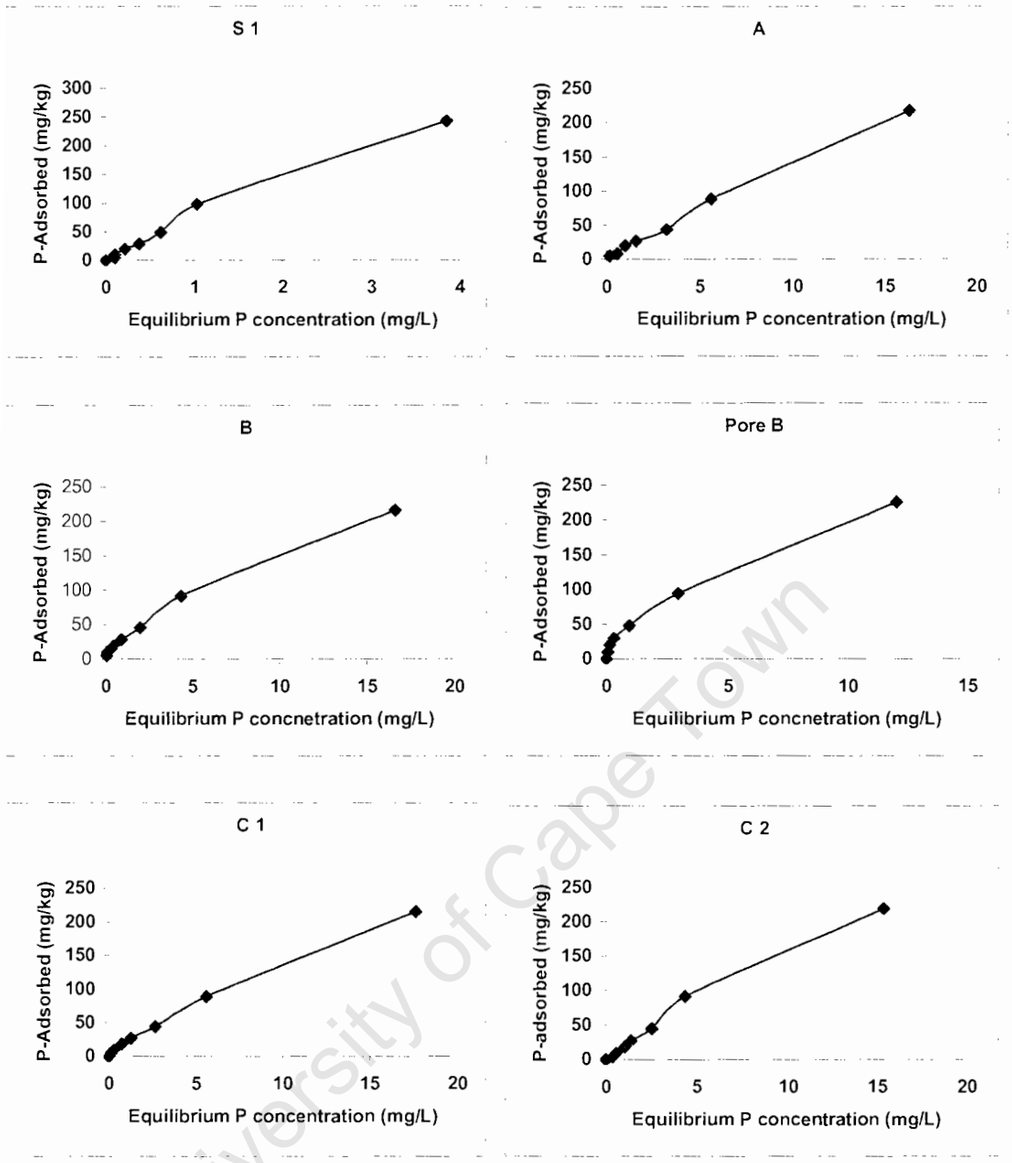
$$ECEC = [Ca^{2+}] + [Mg^{2+}] + [Acidity]$$

B.3 Base saturation

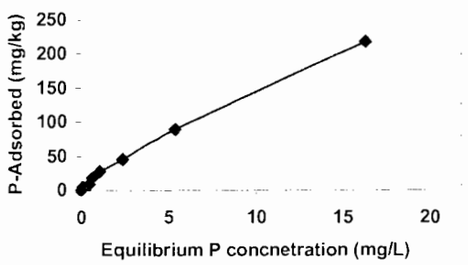
Base saturation was calculated using the KCl extractable acidity, and Ca^{2+} and Mg^{2+} concentrations according to the following equation.

$$\text{Base saturation \%} = ([Ca^{2+}] + [Mg^{2+}]) / ECEC \times 100$$

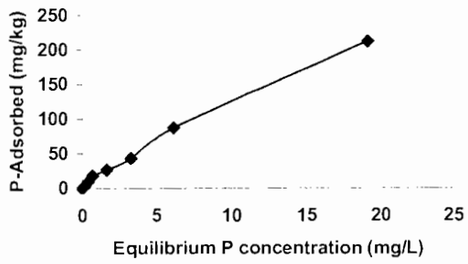
Appendix D. Phosphate Adsorption Isotherms



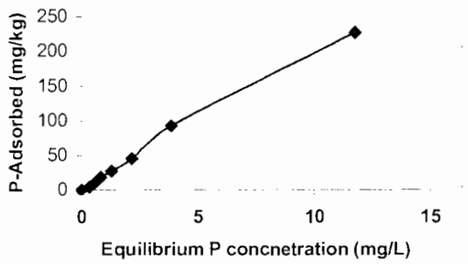
S 24



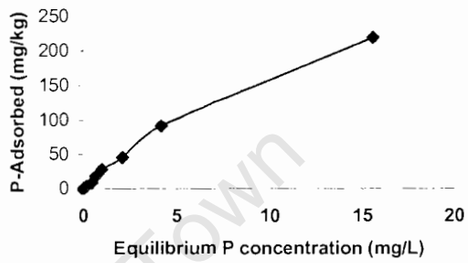
S 26



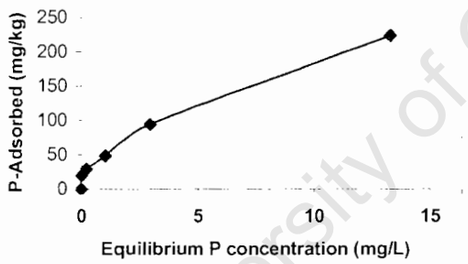
S 27



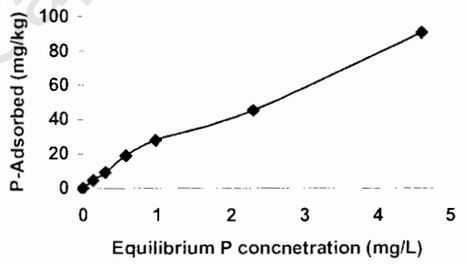
S 28

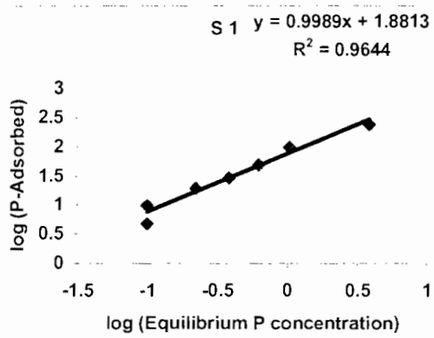


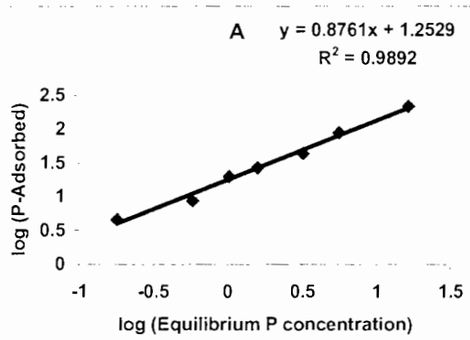
S 29

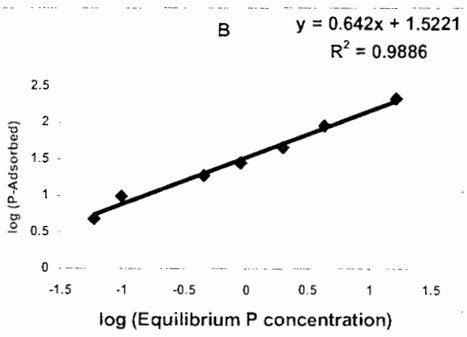


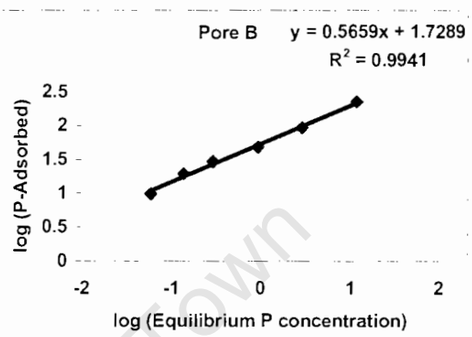
S 30

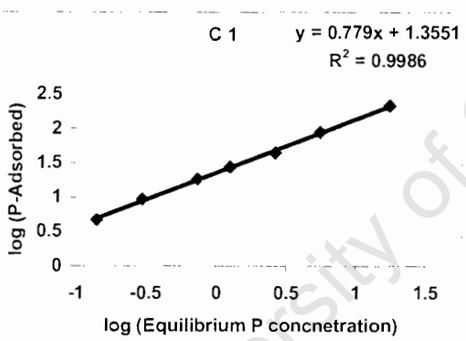


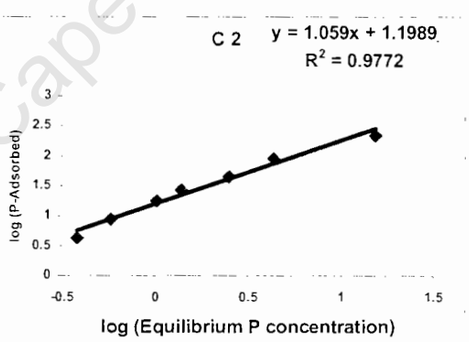


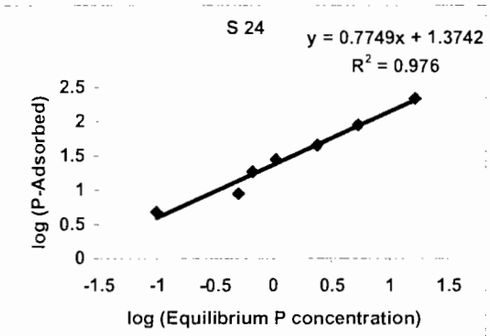


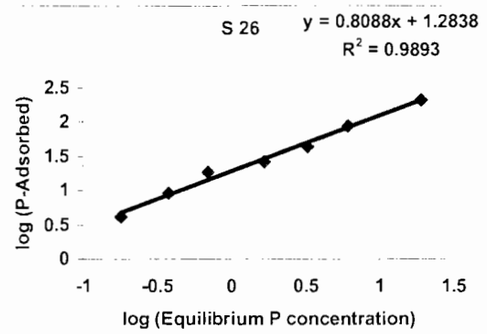


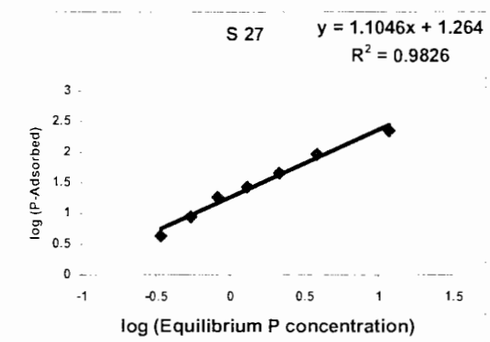


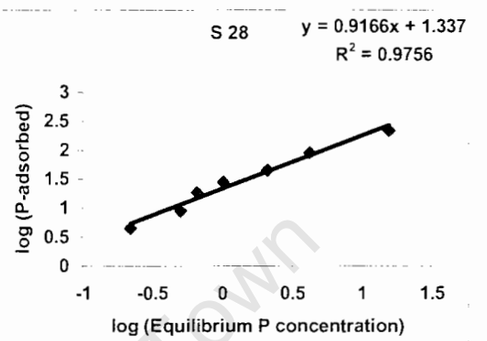


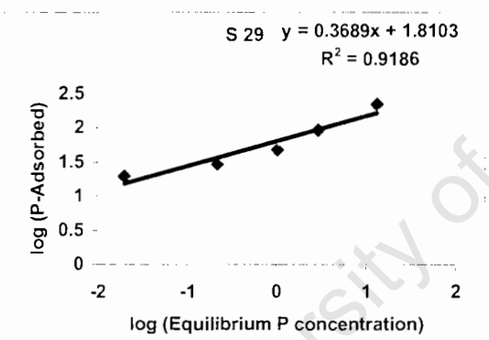


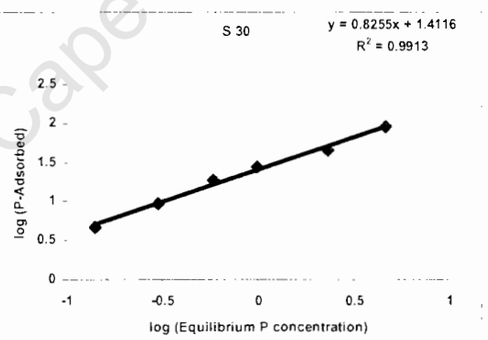




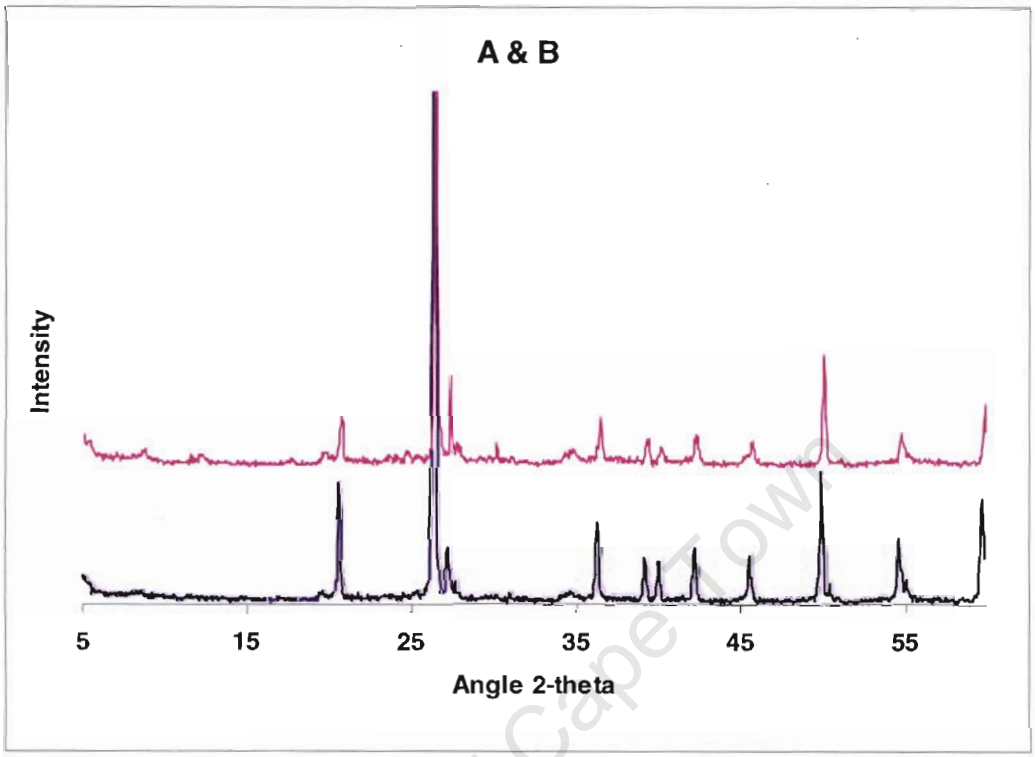


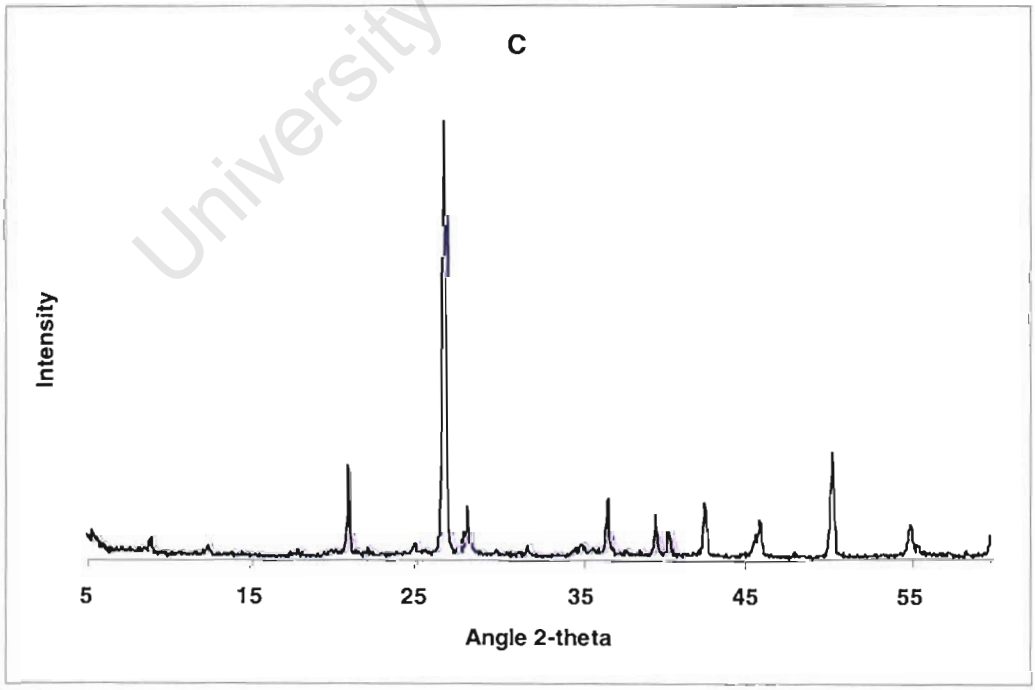


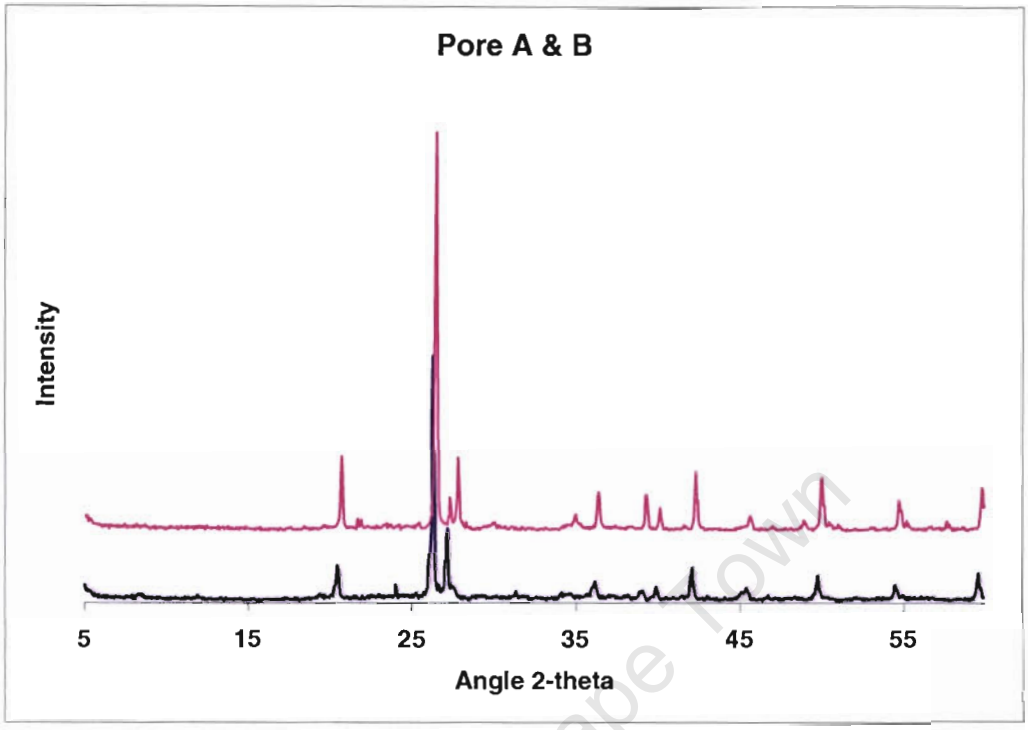


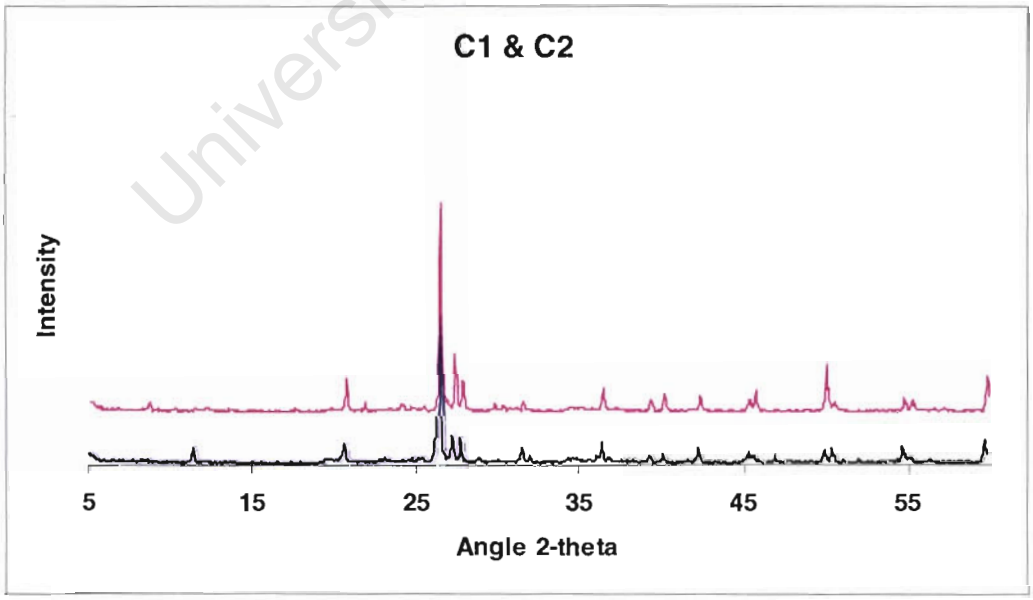


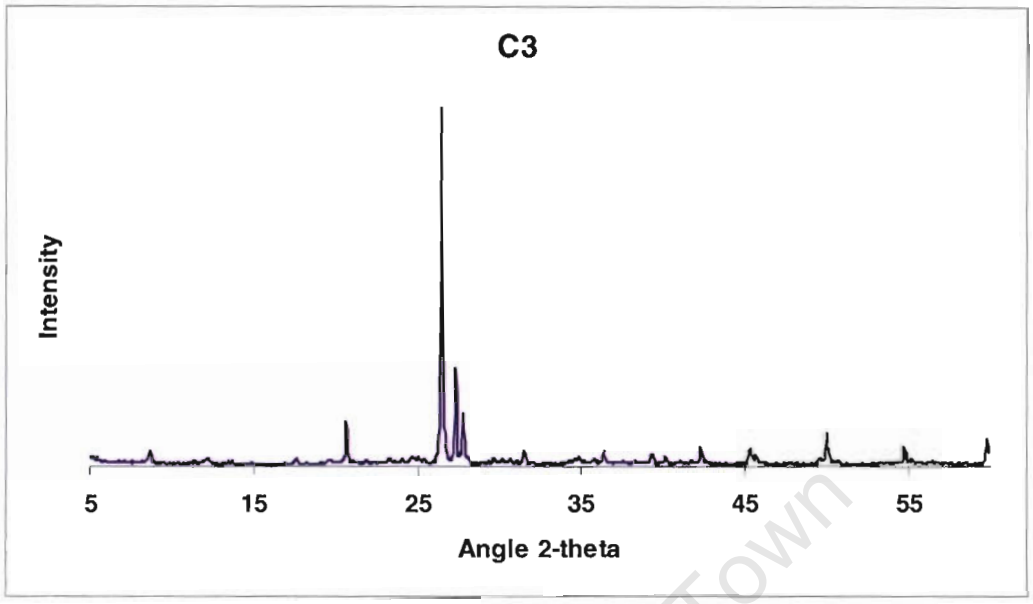
Appendix E XRD Scans

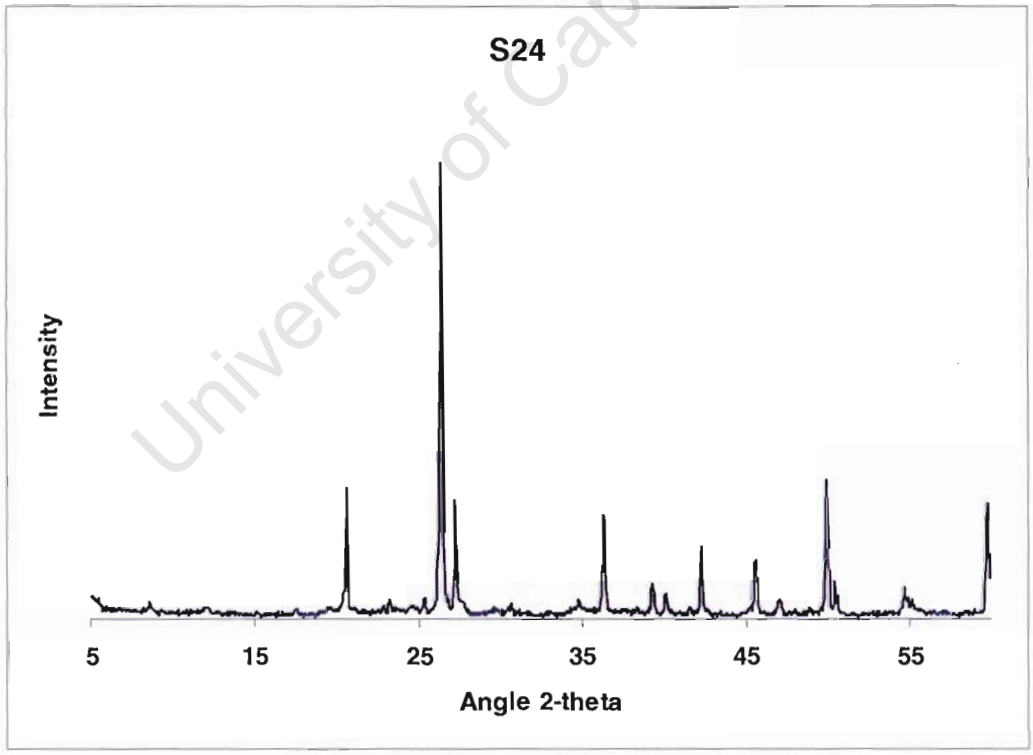


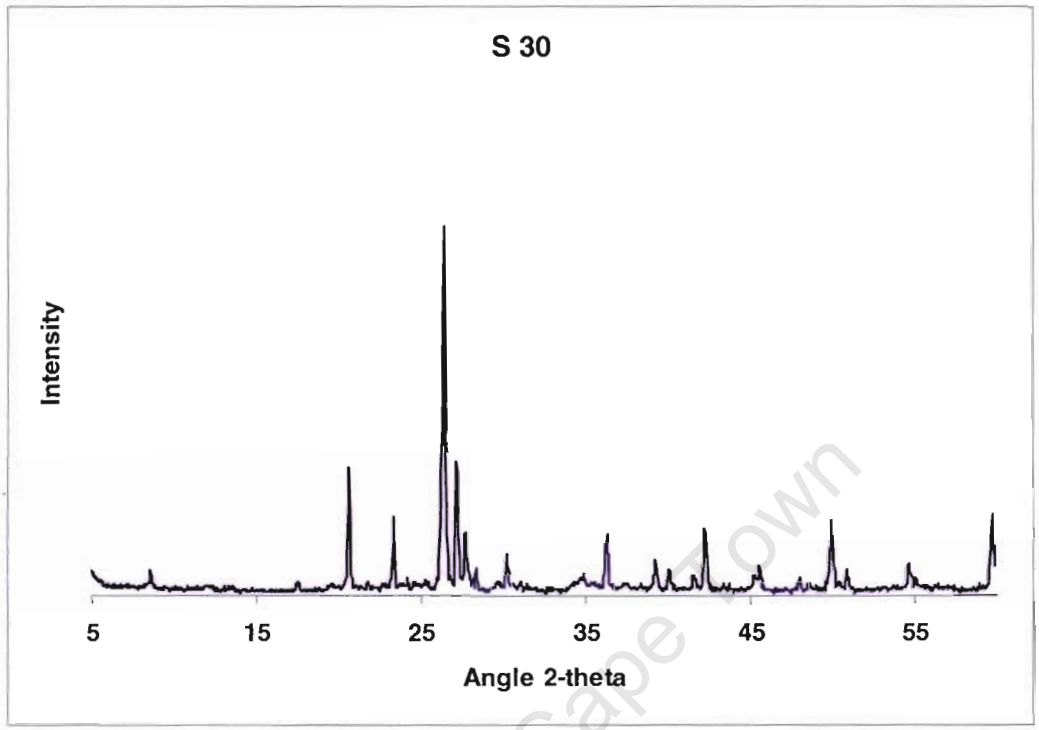


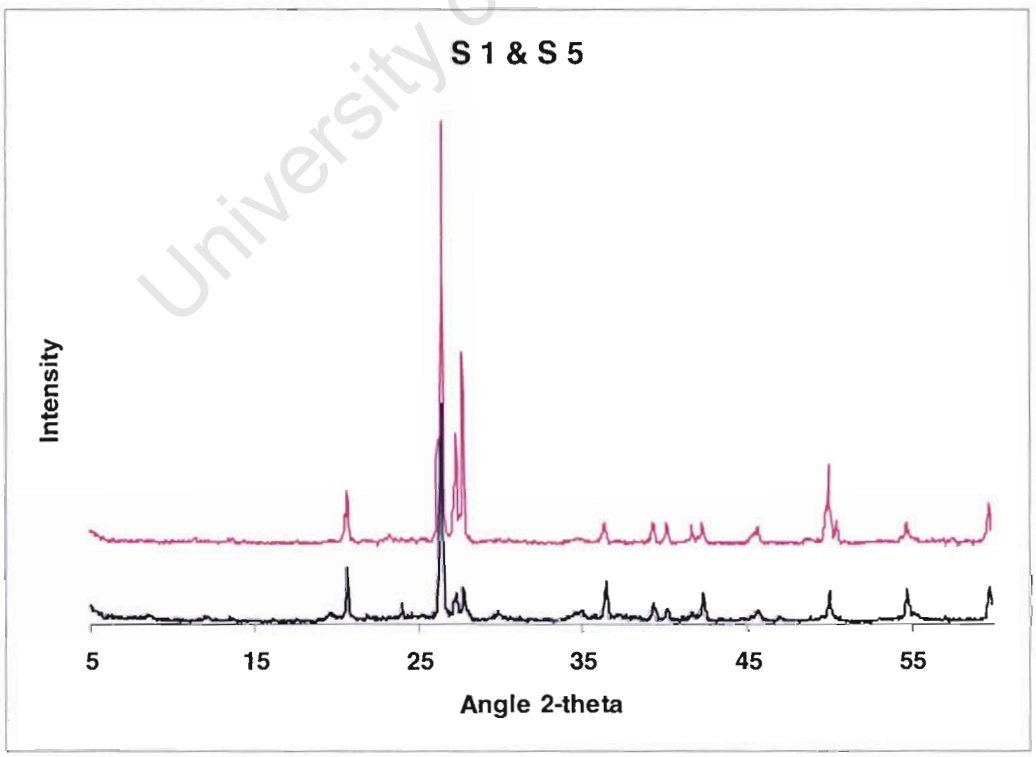












Appendix F – PHREEQC Data

```
Input file: C:\Documents and Settings\EDDavLuc1\My Documents\G10.pqi
Output file: C:\Documents and Settings\EDDavLuc1\My Documents\G10.pqo
Database file: C:\Program Files\USGS\Phreeqc Interactive
2.7.1\phreeqc.dat

------------------
Reading data base.
------------------

SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
PHASES
EXCHANGE_MASTER_SPECIES
EXCHANGE_SPECIES
SURFACE_MASTER_SPECIES
SURFACE_SPECIES
RATES
END
-----------------------------------
Reading input data for simulation 1.
-----------------------------------

DATABASE C:\Program Files\USGS\Phreeqc Interactive 2.7.1\phreeqc.dat
SOLUTION 1 G10
          temp      22.2
          pH        6.8
          pe        6.91
          redox     pe
          units     mg/l
          density   1
          Cl        2218
          P         6.6
          S(6)      422
          N(5)      0
          Fe        0.32
          Na        1289
          Ca        143
          K         55
          Mg        143
          Al        0.004
          Si        23.19
          Sr        1.08
          Zn        0.026
          Ba        0.044
          Cu        0.007
          Alkalinity 183
          B         1.7
          Li        0.0079
          Mn        0.002
          F         1.67
          water     1 # kg
```

```
-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 1.     G10

-----------------------------Solution composition------------------------

      Elements            Molality        Moles

      Al                1.489e-007    1.489e-007
      Alkalinity        3.673e-003    3.673e-003
      B                 1.580e-004    1.580e-004
      Ba                3.218e-007    3.218e-007
      Ca                3.584e-003     3.584e-003
      Cl                6.284e-002    6.284e-002
      Cu                1.107e-007    1.107e-007
      F                 8.830e-005    8.830e-005
      Fe                5.756e-006    5.756e-006
      K                 1.413e-003    1.413e-003
      Li                1.144e-006    1.144e-006
      Mg                5.908e-003    5.908e-003
      Mn                3.657e-008    3.657e-008
      Na                5.632e-002    5.632e-002
      P                 2.140e-004    2.140e-004
      S(6)              4.413e-003    4.413e-003
      Si                3.877e-004    3.877e-004
      Sr                1.238e-005    1.238e-005
      Zn                3.995e-007    3.995e-007

----------------------------Description of solution----------------------

                                    pH  =    6.800
                                    pe  =    6.910
                       Activity of water  =    0.998
                          Ionic strength  =  8.531e-002
                       Mass of water (kg)  =  1.000e+000
                   Total carbon (mol/kg)  =  4.505e-003
                      Total CO2 (mol/kg)  =  4.505e-003
                     Temperature (deg C)  =   22.200
                  Electrical balance (eq)  =  1.108e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =    0.75
                              Iterations  =   10
                                 Total H  = 1.110193e+002
                                 Total O  = 5.553931e+001
```

----------Distribution of species----------

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.903e-007	1.585e-007	-6.720	-6.800	-0.080
OH-	6.561e-008	5.083e-008	-7.183	-7.294	-0.111
H2O	5.551e+001	9.976e-001	1.744	-0.001	0.000
Al	1.489e-007				
Al(OH)4-	5.336e-008	4.223e-008	-7.273	-7.374	-0.102
AlF2+	5.152e-008	4.077e-008	-7.288	-7.390	-0.102
AlF3	2.939e-008	2.997e-008	-7.532	-7.523	0.009
Al(OH)2+	6.201e-009	4.907e-009	-8.208	-8.309	-0.102
Al(OH)3	3.618e-009	3.690e-009	-8.442	-8.433	0.009
AlF+2	3.595e-009	1.410e-009	-8.444	-8.851	-0.406
AlF4-	8.821e-010	6.981e-010	-9.054	-9.156	-0.102
AlOH+2	3.251e-010	1.275e-010	-9.488	-9.894	-0.406
Al+3	1.273e-011	2.449e-012	-10.895	-11.611	-0.716
AlSO4+	1.176e-011	9.303e-012	-10.930	-11.031	-0.102
AlF5-2	1.661e-012	6.516e-013	-11.780	-12.186	-0.406
Al(SO4)2-	4.571e-013	3.617e-013	-12.340	-12.442	-0.102
AlF6-3	3.315e-016	4.035e-017	-15.480	-16.394	-0.915
AlHSO4+2	3.255e-019	1.277e-019	-18.487	-18.894	-0.406
B	1.580e-004				
H3BO3	1.573e-004	1.604e-004	-3.803	-3.795	0.009
H2BO3-	6.988e-007	5.531e-007	-6.156	-6.257	-0.102
BF(OH)3-	4.586e-009	3.630e-009	-8.339	-8.440	-0.102
BF2(OH)2-	4.588e-012	3.631e-012	-11.338	-11.440	-0.102
BF3OH-	4.928e-017	3.900e-017	-16.307	-16.409	-0.102
BF4-	1.874e-021	1.483e-021	-20.727	-20.829	-0.102
Ba	3.218e-007				
Ba+2	2.564e-007	1.019e-007	-6.591	-6.992	-0.400
BaSO4	6.241e-008	6.365e-008	-7.205	-7.196	0.009
BaHCO3+	3.006e-009	2.379e-009	-8.522	-8.624	-0.102
BaCO3	3.623e-011	3.695e-011	-10.441	-10.432	0.009
BaOH+	2.748e-014	2.174e-014	-13.561	-13.663	-0.102
C(4)	4.505e-003				
HCO3-	3.329e-003	2.659e-003	-2.478	-2.575	-0.098
CO2	9.662e-004	9.854e-004	-3.015	-3.006	0.009
MgHCO3+	8.570e-005	6.782e-005	-4.067	-4.169	-0.102
NaHCO3	6.502e-005	6.631e-005	-4.187	-4.178	0.009
CaHCO3+	5.331e-005	4.258e-005	-4.273	-4.371	-0.098
CO3-2	1.823e-006	7.421e-007	-5.739	-6.130	-0.390
CaCO3	1.522e-006	1.552e-006	-5.818	-5.809	0.009
MgCO3	1.467e-006	1.496e-006	-5.834	-5.825	0.009
NaCO3-	6.714e-007	5.313e-007	-6.173	-6.275	-0.102
SrHCO3+	2.125e-007	1.698e-007	-6.673	-6.770	-0.098
ZnHCO3+	4.778e-008	3.781e-008	-7.321	-7.422	-0.102
FeHCO3+	2.206e-008	1.746e-008	-7.656	-7.758	-0.102
ZnCO3	1.640e-008	1.673e-008	-7.785	-7.777	0.009
MnHCO3+	3.426e-009	2.711e-009	-8.465	-8.567	-0.102
BaHCO3-	3.006e-009	2.379e-009	-8.522	-8.624	-0.102
SrCO3	1.964e-009	2.003e-009	-8.707	-8.698	0.009

FeCO3	1.146e-009	1.169e-009	-8.941	-8.932	0.009
Zn(CO3)2-2	6.766e-010	2.654e-010	-9.170	-9.576	-0.406
MnCO3	6.612e-010	6.743e-010	-9.180	-9.171	0.009
BaCO3	3.623e-011	3.695e-011	-10.441	-10.432	0.009
Ca	3.584e-003				
Ca+2	3.197e-003	1.313e-003	-2.495	-2.882	-0.386
CaSO4	3.117e-004	3.179e-004	-3.506	-3.498	0.009
CaHCO3+	5.331e-005	4.258e-005	-4.273	-4.371	-0.098
CaHPO4	1.659e-005	1.692e-005	-4.780	-4.772	0.009
CaH2PO4+	2.583e-006	2.044e-006	-5.588	-5.689	-0.102
CaCO3	1.522e-006	1.552e-006	-5.818	-5.809	0.009
CaF+	7.923e-007	6.270e-007	-6.101	-6.203	-0.102
CaPO4-	3.026e-007	2.394e-007	-6.519	-6.621	-0.102
CaOH+	1.734e-009	1.372e-009	-8.761	-8.863	-0.102
CaHSO4+	3.605e-010	2.853e-010	-9.443	-9.545	-0.102
Cl	6.284e-002				
Cl-	6.284e-002	4.883e-002	-1.202	-1.311	-0.110
ZnCl+	1.656e-008	1.311e-008	-7.781	-7.883	-0.102
FeCl+	5.591e-009	4.425e-009	-8.252	-8.354	-0.102
MnCl+	2.875e-009	2.275e-009	-8.541	-8.643	-0.102
ZnCl2	6.496e-010	6.625e-010	-9.187	-9.179	0.009
MnCl2	4.755e-011	4.849e-011	-10.323	-10.314	0.009
ZnCl3-	4.509e-011	3.568e-011	-10.346	-10.448	-0.102
ZnCl4-2	2.177e-012	8.538e-013	-11.662	-12.069	-0.406
MnCl3-	8.240e-013	6.521e-013	-12.084	-12.186	-0.102
FeCl+2	1.500e-013	5.885e-014	-12.824	-13.230	-0.406
FeCl2+	1.774e-014	1.404e-014	-13.751	-13.853	-0.102
FeCl3	6.720e-017	6.854e-017	-16.173	-16.164	0.009
Cu(1)	2.607e-012				
Cu+	2.607e-012	1.980e-012	-11.584	-11.703	-0.119
Cu(2)	1.107e-007				
Cu+2	7.486e-008	3.148e-008	-7.126	-7.502	-0.376
Cu(OH)2	2.556e-008	2.606e-008	-7.592	-7.584	0.009
CuSO4	7.701e-009	7.854e-009	-8.113	-8.105	0.009
CuOH+	2.536e-009	1.982e-009	-8.596	-8.703	-0.107
Cu(OH)3-	1.249e-014	9.886e-015	-13.903	-14.005	-0.102
Cu(OH)4-2	3.166e-020	1.242e-020	-19.500	-19.906	-0.406
F	8.830e-005				
F-	7.558e-005	5.855e-005	-4.122	-4.232	-0.111
MgF+	1.024e-005	8.105e-006	-4.990	-5.091	-0.102
NaF	1.465e-006	1.494e-006	-5.834	-5.826	0.009
CaF+	7.923e-007	6.270e-007	-6.101	-6.203	-0.102
AlF2+	5.152e-008	4.077e-008	-7.288	-7.390	-0.102
AlF3	2.939e-008	2.997e-008	-7.532	-7.523	0.009
HF	1.298e-008	1.324e-008	-7.887	-7.878	0.009
BF(OH)3-	4.586e-009	3.630e-009	-8.339	-8.440	-0.102
AlF+2	3.595e-009	1.410e-009	-8.444	-8.851	-0.406
AlF4-	8.821e-010	6.981e-010	-9.054	-9.156	-0.102
FeF+	4.857e-011	3.844e-011	-10.314	-10.415	-0.102
FeF2+	1.105e-011	8.744e-012	-10.957	-11.058	-0.102
FeF+2	9.890e-012	3.879e-012	-11.005	-11.411	-0.406
MnF+	5.855e-012	4.634e-012	-11.232	-11.334	-0.102

BF2(OH)2-	4.588e-012	3.631e-012	-11.338	-11.440	-0.102
HF2-	3.673e-012	2.907e-012	-11.435	-11.537	-0.102
AlF5-2	1.661e-012	6.516e-013	-11.780	-12.186	-0.406
FeF3	7.880e-013	8.036e-013	-12.103	-12.095	0.009
AlF6-3	3.315e-016	4.035e-017	-15.480	-16.394	-0.915
BF3OH-	4.928e-017	3.900e-017	-16.307	-16.409	-0.102
BF4-	1.874e-021	1.483e-021	-20.727	-20.829	-0.102
SiF6-2	5.073e-026	1.990e-026	-25.295	-25.701	-0.406
Fe(2)	2.076e-007				
Fe+2	1.561e-007	6.565e-008	-6.807	-7.183	-0.376
FeHCO3+	2.206e-008	1.746e-008	-7.656	-7.758	-0.102
FeSO4	1.354e-008	1.381e-008	-7.868	-7.860	0.009
FeHPO4	6.348e-009	6.474e-009	-8.197	-8.189	0.009
FeCl+	5.591e-009	4.425e-009	-8.252	-8.354	-0.102
FeH2PO4+	2.671e-009	2.114e-009	-8.573	-8.675	-0.102
FeCO3	1.146e-009	1.169e-009	-8.941	-8.932	0.009
FeOH+	1.337e-010	1.058e-010	-9.874	-9.976	-0.102
FeF+	4.857e-011	3.844e-011	-10.314	-10.415	-0.102
FeHSO4-	1.802e-014	1.426e-014	-13.744	-13.846	-0.102
Fe(3)	5.548e-006				
Fe(OH)2+	3.554e-006	2.813e-006	-5.449	-5.551	-0.102
Fe(OH)3	1.977e-006	2.016e-006	-5.704	-5.695	0.009
Fe(OH)4-	1.306e-008	1.033e-008	-7.884	-7.986	-0.102
FeOH+2	3.830e-009	1.502e-009	-8.417	-8.823	-0.406
FeF2+	1.105e-011	8.744e-012	-10.957	-11.058	-0.102
FeF+2	9.890e-012	3.879e-012	-11.005	-11.411	-0.406
FeH2PO4+2	1.924e-012	7.547e-013	-11.716	-12.122	-0.406
FeF3	7.880e-013	8.036e-013	-12.103	-12.095	0.009
FeSO4+	7.077e-013	5.601e-013	-12.150	-12.252	-0.102
FeHPO4+	3.353e-013	2.654e-013	-12.475	-12.576	-0.102
Fe+3	2.268e-013	4.365e-014	-12.644	-13.360	-0.716
FeCl+2	1.500e-013	5.885e-014	-12.824	-13.230	-0.406
Fe(SO4)2-	1.908e-014	1.510e-014	-13.719	-13.821	-0.102
FeCl2+	1.774e-014	1.404e-014	-13.751	-13.853	-0.102
Fe2(OH)2-4	2.884e-015	6.825e-017	-14.540	-16.166	-1.626
FeCl3	6.720e-017	6.854e-017	-16.173	-16.164	0.009
Fe3(OH)4-5	1.807e-017	5.206e-020	-16.743	-19.284	-2.540
FeHSO4-2	6.073e-019	2.382e-019	-19.217	-18.623	-0.406
H(0)	5.429e-031				
H2	2.715e-031	2.768e-031	-30.566	-30.558	0.009
K	1.413e-003				
K+	1.401e-003	1.089e-003	-2.853	-2.963	-0.110
KSO4-	1.146e-005	9.072e-006	-4.941	-5.042	-0.102
KHPO4-	6.645e-008	5.259e-008	-7.178	-7.279	-0.102
KOH	2.330e-011	2.376e-011	-10.633	-10.624	0.009
Li	1.144e-006				
Li+	1.137e-006	9.159e-007	-5.944	-6.038	-0.094
LiSO4-	6.294e-009	4.981e-009	-8.201	-8.303	-0.102
LiOH	1.295e-013	1.321e-013	-12.888	-12.879	0.009

Mg	5.908e-003				
Mg+2	5.180e-003	2.205e-003	-2.286	-2.657	-0.371
MgSO4	5.872e-004	5.988e-004	-3.231	-3.223	0.009
MgHCO3+	8.570e-005	6.782e-005	-4.067	-4.169	-0.102
MgHPO4	3.766e-005	3.841e-005	-4.424	-4.416	0.009
MgF+	1.024e-005	8.105e-006	-4.990	-5.091	-0.102
MgH2PO4+	5.524e-006	4.371e-006	-5.258	-5.359	-0.102
MgCO3	1.467e-006	1.496e-006	-5.834	-5.825	0.009
MgPO4-	6.854e-007	5.424e-007	-6.164	-6.266	-0.102
MgOH+	4.934e-008	3.905e-008	-7.307	-7.408	-0.102
Mn(2)	3.657e-008				
Mn+2	2.720e-008	1.144e-008	-7.565	-7.942	-0.376
MnHCO3+	3.426e-009	2.711e-009	-8.465	-8.567	-0.102
MnCl+	2.875e-009	2.275e-009	-8.541	-8.643	-0.102
MnSO4	2.354e-009	2.401e-009	-8.628	-8.620	0.009
MnCO3	6.612e-010	6.743e-010	-9.180	-9.171	0.009
MnCl2	4.755e-011	4.849e-011	-10.323	-10.314	0.009
MnF+	5.855e-012	4.634e-012	-11.232	-11.334	-0.102
MnOH+	1.857e-012	1.470e-012	-11.731	-11.833	-0.102
MnCl3-	8.240e-013	6.521e-013	-12.084	-12.186	-0.102
Mn(3)	1.562e-026				
Mn+3	1.562e-026	1.902e-027	-25.806	-26.721	-0.915
Na	5.632e-002				
Na+	5.591e-002	4.434e-002	-1.253	-1.353	-0.101
NaSO4-	3.436e-004	2.719e-004	-3.464	-3.566	-0.102
NaHCO3	6.502e-005	6.631e-005	-4.187	-4.178	0.009
NaHPO4-	2.706e-006	2.142e-006	-5.568	-5.669	-0.102
NaF	1.465e-006	1.494e-006	-5.834	-5.826	0.009
NaCO3-	6.714e-007	5.313e-007	-6.173	-6.275	-0.102
NaOH	1.808e-009	1.844e-009	-8.743	-8.734	0.009
O(0)	1.300e-032				
O2	6.498e-033	6.627e-033	-32.187	-32.179	0.009
P	2.140e-004				
H2PO4-	8.152e-005	6.424e-005	-4.089	-4.192	-0.103
HPO4-2	6.639e-005	2.477e-005	-4.178	-4.606	-0.428
MgHPO4	3.766e-005	3.841e-005	-4.424	-4.416	0.009
CaHPO4	1.659e-005	1.692e-005	-4.780	-4.772	0.009
MgH2PO4+	5.524e-006	4.371e-006	-5.258	-5.359	-0.102
NaHPO4-	2.706e-006	2.142e-006	-5.568	-5.669	-0.102
CaH2PO4+	2.583e-006	2.044e-006	-5.588	-5.689	-0.102
MgPO4-	6.854e-007	5.424e-007	-6.164	-6.266	-0.102
CaPO4-	3.026e-007	2.394e-007	-6.519	-6.621	-0.102
KHPO4-	6.645e-008	5.259e-008	-7.178	-7.279	-0.102
FeHPO4	6.348e-009	6.474e-009	-8.197	-8.189	0.009
FeH2PO4+	2.671e-009	2.114e-009	-8.573	-8.675	-0.102
PO4-3	6.122e-010	6.659e-011	-9.213	-10.177	-0.963
FeH2PO4-2	1.924e-012	7.547e-013	-11.716	-12.122	-0.406
FeHPO4-	3.353e-013	2.654e-013	-12.475	-12.576	-0.102

S(6)	4.413e-003				
SO4-2	3.157e-003	1.246e-003	-2.501	-2.905	-0.404
MgSO4	5.872e-004	5.988e-004	-3.231	-3.223	0.009
NaSO4-	3.436e-004	2.719e-004	-3.464	-3.566	-0.102
CaSO4	3.117e-004	3.179e-004	-3.506	-3.498	0.009
KSO4-	1.146e-005	9.072e-006	-4.941	-5.042	-0.102
SrSO4	1.058e-006	1.079e-006	-5.975	-5.967	0.009
BaSO4	6.241e-008	6.365e-008	-7.205	-7.196	0.009
ZnSO4	3.165e-008	3.228e-008	-7.500	-7.491	0.009
HSO4-	2.284e-008	1.807e-008	-7.641	-7.743	-0.102
FeSO4	1.354e-008	1.381e-008	-7.868	-7.860	0.009
CuSO4	7.701e-009	7.854e-009	-8.113	-8.105	0.009
LiSO4-	6.294e-009	4.981e-009	-8.201	-8.303	-0.102
MnSO4	2.354e-009	2.401e-009	-8.628	-8.620	0.009
Zn(SO4)2-2	8.517e-010	3.341e-010	-9.070	-9.476	-0.406
CaHSO4+	3.605e-010	2.853e-010	-9.443	-9.545	-0.102
AlSO4+	1.176e-011	9.303e-012	-10.930	-11.031	-0.102
FeSO4+	7.077e-013	5.601e-013	-12.150	-12.252	-0.102
Al(SO4)2-	4.571e-013	3.617e-013	-12.340	-12.442	-0.102
Fe(SO4)2-	1.908e-014	1.510e-014	-13.719	-13.821	-0.102
FeHSO4+	1.802e-014	1.426e-014	-13.744	-13.846	-0.102
FeHSO4+2	6.073e-019	2.382e-019	-18.217	-18.623	-0.406
AlHSO4+2	3.255e-019	1.277e-019	-18.487	-18.894	-0.406
Si	3.877e-004				
H4SiO4	3.873e-004	3.950e-004	-3.412	-3.403	0.009
H3SiO4-	4.205e-007	3.328e-007	-6.376	-6.478	-0.102
H2SiO4-2	3.025e-013	1.187e-013	-12.519	-12.926	-0.406
SiF6-2	5.073e-026	1.990e-026	-25.295	-25.701	-0.406
Sr	1.238e-005				
Sr+2	1.111e-005	4.593e-006	-4.954	-5.338	-0.384
SrSO4	1.058e-006	1.079e-006	-5.975	-5.967	0.009
SrHCO3+	2.125e-007	1.698e-007	-6.673	-6.770	-0.098
SrCO3	1.964e-009	2.003e-009	-8.707	-8.698	0.009
SrOH+	1.867e-012	1.483e-012	-11.729	-11.829	-0.100
Zn	3.995e-007				
Zn+2	2.841e-007	1.130e-007	-6.547	-6.947	-0.400
ZnHCO3-	4.778e-008	3.781e-008	-7.321	-7.422	-0.102
ZnSO4	3.165e-008	3.228e-008	-7.500	-7.491	0.009
ZnCl+	1.656e-008	1.311e-008	-7.781	-7.883	-0.102
ZnCO3	1.640e-008	1.673e-008	-7.785	-7.777	0.009
Zn(SO4)2-2	8.517e-010	3.341e-010	-9.070	-9.476	-0.406
ZnOH+	7.951e-010	6.292e-010	-9.100	-9.201	-0.102
Zn(CO3)2-2	6.766e-010	2.654e-010	-9.170	-9.576	-0.406
ZnCl2	6.496e-010	6.625e-010	-9.187	-9.179	0.009
Zn(OH)2	5.525e-011	5.635e-011	-10.258	-10.249	0.009
ZnCl3-	4.509e-011	3.568e-011	-10.346	-10.448	-0.102
ZnCl4-2	2.177e-012	8.538e-013	-11.662	-12.069	-0.406
Zn(OH)3-	1.417e-015	1.122e-015	-14.849	-14.950	-0.102
Zn(OH)4-2	2.853e-021	1.119e-021	-20.545	-20.951	-0.406

```
-------------------------------Saturation indices-----------------------

Phase                SI log IAP  log KT

Al(OH)3(a)        -2.20    8.79   10.98  Al(OH)3
Albite            -0.75    4.03    4.78  NaAlSi3O8
Alunite           -1.76   -2.81   -1.05  KAl3(SO4)2(OH)6
Anhydrite         -1.44   -5.79   -4.35  CaSO4
Anorthite         -4.63   21.49   26.12  CaAl2Si2O8
Aragonite         -0.69   -9.01   -8.32  CaCO3
Barite             0.12   -9.90  -10.02  BaSO4
Ca-Montmorillonite   1.70    9.76    8.06  Ca0.165Al2.33Si3.67O10(OH)2
Calcite           -0.55   -9.01   -8.46  CaCO3
Celestite         -1.62   -8.24   -6.63  SrSO4
Chalcedony         0.18   -3.40   -3.58  SiO2
Chlorite(14A)     -7.35   62.08   69.43  Mg5Al2Si3O10(OH)8
Chrysotile        -6.53   26.02   32.55  Mg3Si2O5(OH)4
CO2(g)            -1.57  -19.73  -18.16  CO2
Dolomite          -0.77  -17.80  -17.02  CaMg(CO3)2
Fe(OH)3(a)         2.15   20.12   17.98  Fe(OH)3
Fluorite          -0.71  -11.35  -10.63  CaF2
Gibbsite           0.52    8.79    8.27  Al(OH)3
Goethite           7.94   20.13   12.19  FeOOH
Gypsum            -1.21   -5.79   -4.58  CaSO4:2H2O
H2(g)            -27.42  -27.42    0.00  H2
H2O(g)            -1.58   -0.00    1.58  H2O
Halite            -4.24   -2.66    1.58  NaCl
Hausmannite      -17.34   44.39   61.73  Mn3O4
Hematite          17.87   40.25   22.38  Fe2O3
Hydroxyapatite     2.14  -38.14  -40.28  Ca5(PO4)3OH
Illite             1.18   13.34   12.16  K0.6Mg0.25Al2.3Si3.5O10(OH)2
Jarosite-K         0.93   31.20   30.27  KFe3(SO4)2(OH)6
K-feldspar         0.25    2.42    2.17  KAlSi3O8
K-mica             6.88   19.99   13.12  KAl3Si3O10(OH)2
Kaolinite          3.09   10.77    7.68  Al2Si2O5(OH)4
Manganite         -5.97   19.37   25.34  MnOOH
Melanterite       -7.85  -10.09   -2.24  FeSO4:7H2O
O2(g)            -29.23   54.84   84.07  O2
Pyrochroite       -9.54    5.66   15.20  Mn(OH)2
Pyrolusite        -8.76   33.08   41.83  MnO2
Quartz             0.62   -3.40   -4.02  SiO2
Rhodochrosite     -2.95  -14.07  -11.12  MnCO3
Sepiolite         -4.16   11.68   15.83  Mg2Si3O7.5OH:3H2O
Sepiolite(d)      -6.98   11.68   18.66  Mg2Si3O7.5OH:3H2O
Siderite          -2.44  -13.31  -10.87  FeCO3
SiO2(a)           -0.67   -3.40   -2.74  SiO2
Smithsonite       -3.11  -13.08   -9.97  ZnCO3
Strontianite      -2.20  -11.47   -9.27  SrCO3
Talc              -2.50   19.22   21.72  Mg3Si4O10(OH)2
Vivianite         -5.91  -41.91  -36.00  Fe3(PO4)2:8H2O
Willemite         -5.66    9.90   15.56  Zn2SiO4
Witherite         -4.55  -13.12   -8.57  BaCO3
Zn(OH)2(e)        -4.85    6.65   11.50  Zn(OH)2

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End of simulation.
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Appendix G

DWAF Guideline concentrations for usage of waters
(Adapted from South African Water Quality Guidelines)

	Domestic use	Agricultural Use: Irrigation	Agricultural Use: Livestock Watering
pH	6.0 – 9.0	6.5 – 8.4	
EC	0 – 70 mS/m	< 40 mS/m	
TDS	0 – 450 mg/L		0 – 1000 mg/L
Na^+	0 – 100 mg/L	< 70 mg/L	0 –2000 mg/L
NH_4^+	0 – 1 mg/L		
K^+	0 – 50 mg/L		
Mg^{2+}	0 – 30 mg/L		
Ca^{2+}	0 – 32 mg/L		0 – 1000 mg/L
F^-	0 –1.0 mg/L	< 2.0 mg/L	0 – 2 mg/L
Cl^-	0 – 100 mg/L	< 100 mg/L	0 – 1500 mg/L
SO_4^{2-}	0 – 200 mg/L		0 – 1000 mg/L
NO_3^-			0 – 100 mg/L
NO_2^-			
DOC	0 – 5 mg/L		
Alkalinity as $CaCO_3$			
Al	0 – 0.15 mg/L	< 5.0 mg/L	0 – 5 mg/L
As	0 – 10 µg/L	< 0.1 mg/L	0 – 1.0 mg/L
B		< 0.5 mg/L	0 – 5 mg/L
Cd	0 – 5 µg/L	< 0.01 mg/L	0 – 0.01 mg/L
Co		< 0.05 mg/L	0 – 1 mg/L
Cr	0 – 0.05 mg/L	< 0.10 mg/L	0 – 1 mg/L
Cu	0 – 1 mg/L	< 0.2 mg/L	0 – 0.5 mg/L
Fe	0 – 0.1 mg/L	< 5.0 mg/L	0 – 10 mg/L
Li		< 2.5 mg/L	
Mg			0 – 500 mg/L
Mn	0 – 0.05 mg/L	< 0.02 mg/L	0 – 10 mg/L
Mo		< 0.01 mg/L	0 – 0.01 mg/L
Ni		< 0.20 mg/L	0 – 1 mg/L
Pb	0 –10 µg/L	< 0.2 mg/L	0 – 0.1 mg/L
Se	0 –20 µg/L	< 0.02 mg/L	0 – 50 µg/L
Si			
Th	0 –0.228 Bq/L		
U	0 – 0.07 mg/L	< 0.01 mg/L	
Zn	0 – 3 mg/L	< 1.0 mg/L	0 – 20 mg/L
SAR		< 2.0 mg/L	

Appendix H

Table H1:Speciation of some elements for water samples

Elemental concentrations expressed in molality and speciation as a percentage.

Elements	Raw Effluent	Pond Effluent	Cut off trench	Seepage pond (SP)	SP Pore Water A	SP Pore Water B
Al	5.373×10^{-2}	3.471×10^{-2}	1.736×10^{-2}	-	-	-
$AlSO_4^+$	56.2	65	62.3	-	-	-
$Al(SO_4)^{2-}$	29.6	16.7	20.5	-	-	-
Al^{+3}	7.4	14.6	10.7	-	-	-
B	1.043×10^{-4}	-	9.318×10^{-4}	8.357×10^{-4}	1.376×10^{-3}	8.040×10^{-4}
H_3BO_3	100	-	100	86.7	99.3	99.3
$H_2BO_3^-$	-	-	-	13.3	0.7	0.7
Ba	1.043×10^{-4}	3.273×10^{-6}	-	-	-	-
$BaSO_4$	64.8	54.9	-	-	-	-
Ba^{+2}	35.2	45.1	-	-	-	-
Ca	8.441×10^{-3}	9.927×10^{-3}	1.008×10^{-2}	1.687×10^{-2}	9.700×10^{-3}	1.132×10^{-2}
Ca^{+2}	48.1	65.9	60.4	62.5	47.0	60.0
$CaSO_4$	41.8	33.0	39.6	35.5	53.0	40.0
Cl	1.286×10^{-2}	3.076×10^{-3}	2.079×10^{-2}	1.927×10^{-1}	2.784×10^{-1}	2.574×10^{-1}
Cl^-	98.9	99.1	99.9	100	100	100
$FeCl^+$	0.9	0.8	-	-	-	-
F	1.174×10^{-3}	1.279×10^{-3}	9.111×10^{-4}	-	-	-
AlF^{+2}	91.5	97.6	95.5	-	-	-
AlF_2^+	4.1	1.2	2.2	-	-	-
Fe(2)	5.300×10^{-2}	2.694×10^{-2}	-	-	-	-
Fe^{+2}	49.7	68.9	-	-	-	-
$FeSO_4$	39.7	29.9	-	-	-	-
K	8.023×10^{-3}	6.577×10^{-3}	6.343×10^{-3}	3.820×10^{-3}	6.970×10^{-3}	5.300×10^{-3}
K^+	89.8	95.1	93.7	93.8	88.2	92.5
KSO_4^-	10.2	4.9	6.3	6.2	11.8	7.5
Li	-	-	1.017×10^{-4}	-	-	-
Li^+	-	-	95.2	-	-	-
$LiSO_4^-$	-	-	4.8	-	-	-
Mg	2.383×10^{-2}	1.666×10^{-2}	4.080×10^{-2}	3.240×10^{-2}	5.394×10^{-2}	3.583×10^{-2}
$MgSO_4$	54.5	36.7	42.2	37.8	55.7	42.8
Mg^{+2}	45.5	63.3	57.8	60.4	44.3	57.2
Mn (2)	4.221×10^{-4}	9.469×10^{-4}	1.242×10^{-3}	-	-	2.301×10^{-4}
Mn^{+2}	55.2	69.6	63.2	-	-	57.0
$MnSO_4$	44.2	30.2	35.0	-	-	29.2
Mn(3)	-	-	-	-	-	-
Mn^{+3}	-	-	-	-	-	-
Na	2.332×10^{-2}	2.074×10^{-2}	6.283×10^{-2}	2.577×10^{-1}	5.225×10^{-2}	3.736×10^{-1}
Na^+	92.4	96.1	94.9	94.4	89.5	93.3
$NaSO_4^-$	7.6	3.9	5.1	5.4	10.5	6.6
P	1.324×10^{-4}	-	-	-	-	-
$FeH_2PO_4^+$	77.9	-	-	-	-	-
$H_2PO_4^-$	18.9	-	-	-	-	-
S(6)	1.919×10^{-1}	8.511×10^{-2}	8.178×10^{-2}	8.611×10^{-2}	1.603×10^{-1}	1.214×10^{-1}
SO_4^{-2}	28.7	32.5	46.6	62.5	74.1	62.8
HSO_4^-	25.9	4.7	-	-	-	-
$AlSO_4^+$	12.5	30.2	13.2	-	-	-
$FeSO_4$	8.7	9.5	-	-	-	-
$Al(SO_4)^{2-}$	6.6	6.8	4.6	-	-	-
$MgSO_4$	5.4	7.2	21.0	14.2	18.8	12.6
Si	1.194×10^{-4}	2.049 x 10-4	6.087×10^{-4}	-	4.071×10^{-4}	3.281×10^{-4}
H_4SiO_4	100	100	100	-	99.8	99.9
Sr	-	-	-	-	-	1.032×10^{-4}
Sr^{+2}	-	-	-	-	-	61.4
$SrSO_4$	-	-	-	-	-	38.6
Zn	1.136×10^{-4}	-	-	-	-	-
Zn^{+2}	52.2	-	-	-	-	-
$ZnSO_4$	35.1	-	-	-	-	-
$Zn(SO_4)_2^{-2}$	12.1	-	-	-	-	-

Table H2:Groundwater Speciation

Elemental concentrations expressed in molality and speciation as a percentage.

Elements	G1	G4	G5	G7	G8	G9
B	6.477×10^{-4}	2.215×10^{-4}	9.032×10^{-4}	4.382×10^{-4}	6.520×10^{-4}	1.860×10^{-4}
H_3BO_3	98.8	98.6	99.6	99.0	98.9	99.2
$H_2BO_3^-$	1.2	1.4	0.4	1.0	1.1	0.7
C	4.924×10^{-3}	5.263×10^{-3}	5.690×10^{-3}	4.040×10^{-3}	4.180×10^{-3}	4.956×10^{-3}
HCO_3^-	78.1	85.4	63.5	73.3	83.4	80.5
CO_2	8.3	7.7	17.9	8.8	9.4	14.6
$MgHCO_3^+$	6.9	2.5	8.2	7.9	3.5	1.9
Ca	1.473×10^{-2}	4.819×10^{-3}	2.139×10^{-2}	1.773×10^{-2}	6.498×10^{-3}	3.762×10^{-3}
Ca^{+2}	85.9	89.3	74.7	87.4	68.4	82.8
$CaSO_4$	12.5	8.2	24.1	11.6	30.0	15.1
Cl	1.090×10^{-1}	8.151×10^{-2}	3.616×10^{-1}	2.756×10^{-1}	2.865×10^{-2}	6.581×10^{-2}
Cl^-	100	100	100	100	100	100-
$FeCl^+$	-	-	-	-	-	
F	1.195×10^{-4}	1.054×10^{-4}	-	1.596×10^{-4}	1.635×10^{-4}	1.365×10^{-4}
F^-	66.1	84	-	60.6	79.8	86.5
MgF^+	30.1	12.7	-	32.9	17.7	10.6
CaF^+	2.1	-	-	1.9	1.1	0.9
K	4.773×10^{-3}	1.338×10^{-3}	5.502×10^{-3}	4.203×10^{-3}	2.469×10^{-3}	1.517×10^{-3}
K^+	98.5	99.2	95.9	98.4	96.2	98.4
KSO_4^-	1.5	0.8	4.1	1.6	3.8	1.6
Mg	2.594×10^{-2}	7.116×10^{-3}	6.011×10^{-2}	3.779×10^{-2}	1.373×10^{-2}	5.995×10^{-3}
$MgSO_4$	14.6	9.4	28.7	14.1	33.4	17.1
Mg^{+2}	83.8	87.8	69.9	84.7	64.8	80.5
Mn (2)	-	-	1.275×10^{-4}	-	-	-
Mn^{+2}	-	-	60.5	-	-	-
$MnCl^+$	-	-	17.9	-	-	-
$MnSO_4$	-	-	15.6	-	-	-
Mn(3)	-	-	-	-	-	-
Mn^{+3}	-	-	-	-	-	-
Na	8.623×10^{-2}	7.858×10^{-2}	4.789×10^{-1}	2.974×10^{-1}	5.409×10^{-2}	6.248×10^{-2}
Na^+	98.7	99.2	96.5	98.6	97.0	98.7
$NaSO_4^-$	1.2	0.6	3.4	1.3	2.8	1.2
P	-	1.819×10^{-4}	9.216×10^{-4}	1.450×10^{-4}	1.948×10^{-4}	1.623×10^{-4}
HPO_4^{-2}	-	42.4	26.0	30.2	35.7	38.4
$MgHPO_4$	-	24.3	31.5	37.0	30.9	18.9
$H_2PO_4^-$	-	15.3	21.4	11.3	16.5	28.8
S(6)	1.454×10^{-2}	5.089×10^{-3}	7.874×10^{-2}	2.368×10^{-2}	2.416×10^{-2}	8.664×10^{-3}
SO_4^{-2}	54.0	69.3	50.5	52.0	66.2	72.9
$NaSO_4^-$	6.8	9.6	20.7	16.5	6.4	8.4
$CaSO_4$	12.7	7.8	6.5	8.7	8.1	6.5
$MgSO_4$	26.0	13.1	21.9	22.5	19.0	11.8
Si	3.845×10^{-4}	1.996×10^{-4}	3.761×10^{-4}	1.636×10^{-4}	3.693×10^{-4}	2.991×10^{-4}
H_4SiO_4	99.7	99.7	99.9	99.8	99.7	99.8

Table H2:Groundwater Speciation (cont.)

Elemental concentrations expressed in molality and speciation as a percentage.

Elements	G 10	G 11	G 12
B	1.580×10^{-4}	1.664×10^{-4}	5.190×10^{-4}
H_3BO_3	99.6	99.5	100
$H_2BO_3^-$	0.4	0.5	-
C	4.505×10^{-3}	3.605×10^{-3}	1.938×10^{-2}
HCO_3^-	73.9	73.9	7.3
CO_2	21.5	21.1	91.5
$MgHCO_3^+$	1.9	2.0	0.5
Ca	3.584×10^{-3}	3.785×10^{-3}	1.058×10^{-2}
Ca^{+2}	89.2	90.1	82.5
$CaSO_4$	8.7	8.2	17.0
Cl	6.284 x 10-2	6.623×10^{-2}	2.032×10^{-1}
Cl^-	100	100	100
K	1.413×10^{-3}	1.259×10^{-3}	3.457×10^{-3}
K^+	99.2	99.2	97.6
KSO_4^-	0.8	0.8	2.4
Mg	5.908×10^{-3}	6.240×10^{-3}	2.429×10^{-2}
$MgSO_4$	9.9	9.5	20.0
Mg^{+2}	87.7	88.5	79.5
Na	5.632×10^{-2}	6.359×10^{-2}	2.355×10^{-1}
Na^+	99.3	99.3	98.1
$NaSO_4^-$	0.6	0.6	1.9
P	2.140×10^{-4}	1.881×10^{-4}	1.313×10^{-4}
HPO_4^{-2}	31.0	31.0	-
$MgHPO_4$	17.6	18.1	13.8
$H_2PO_4^-$	38.1	37.2	77.3
S(6)	4.413×10^{-3}	4.341×10^{-3}	2.693×10^{-2}
SO_4^{-2}	71.5	70.4	58.5
$NaSO_4^-$	7.8	8.5	16.4
$CaSO_4$	7.1	7.2	6.7
$MgSO_4$	13.3	13.6	18.0
Si	3.877×10^{-4}	3.798×10^{-4}	2.032×10^{-4}
H_4SiO_4	99.9	99.9	100

Table H3: Speciation of paste extract samples

Elemental concentrations expressed in molality and speciation as a percentage.

Elements	B	S2	S5	Pore A	S24	S25
B	1.460×10^{-3}	3.180×10^{-4}	1.530×10^{-3}	1.989×10^{-3}	-	6.004×10^{-4}
H_3BO_3	98.6	93.2	95.6	93.3	-	98.3
$H_2BO_3^-$	1.4	6.8	4.4	6.7	-	1.7
Ca	2.74×10^{-2}	5.844×10^{-2}	4.908×10^{-2}	2.214×10^{-2}	4.329×10^{-2}	9.651×10^{-3}
Ca^{+2}	87.5	89.7	83.8	58.2	96.2	74.7
$CaSO_4$	12.5	8.7	13.2	41.8	3.8	25.3
Cl	5.825×10^{-1}	6.859×10^{-1}	7.085×10^{-1}	4.819×10^{-1}	2.201×10^{-1}	2.259×10^{-1}
Cl^-	100	99.9	100	100	100	100
$FeCl^+$	-	-	-	-	-	-
Fe (3)	-	1.191×10^{-4}	-	-	1.398×10^{-4}	-
$Fe(OH)_3$	-	78.7	-	-	77.2	-
$Fe(OH)_2^+$	-	12.5	-	-	17.7	-
K	9.949×10^{-3}	4.679×10^{-3}	8.259×10^{-3}	2.397×10^{-2}	5.180×10^{-3}	4.646 x 10-3
K^+	98.1	98.7	97.9	91.1	99.5	95.9
KSO_4^-	1.9	1.3	2.1	8.9	-	4.1
Li	-	-	-	-	-	-
Li^+	-	-	-	-	-	-
$LiSO_4^-$	-	-	-	-	-	-
Mg	7.359×10^{-2}	2.372×10^{-1}	1.009×10^{-1}	2.400×10^{-1}	4.353×10^{-2}	2.401×10^{-2}
$MgSO_4$	16.4	11.7	17.1	50.2	4.8	30.5
Mg^{+2}	83.6	85.8	78.6	49.8	95.2	6935
Mn (2)	-	2.299×10^{-4}	-	-	-	-
Mn^{+2}	-	63.0	-	-	-	-
$MnSO_4$	-	4.6	-	-	-	-
Mn(3)	-	-	-	-	-	-
Mn^{+3}	-	-	-	-	-	-
Na	5.026×10^{-1}	7.186×10^{-2}	2.841×10^{-1}	3.476×10^{-1}	5.269×10^{-2}	2.937×10^{-1}
Na^+	98.4	98.9	98.2	92.4	99.6	96.8
$NaSO_4^-$	1.6	1.1	1.8	7.6	0.4	3.2
P	-	7.955×10^{-3}	7.837×10^{-3}	-	-	-
$MgPO_4$	-	57.5	-	-	-	-
$MgPO_4^-$	-	17.1	8.6	-	-	-
$MgHPO_4$			46.3	-	-	-
HPO_4^{-2}			22.4	-	-	-
S(6)	4.378×10^{-2}	4.918×10^{-2}	5.148×10^{-2}	2.716×10^{-1}	6.980×10^{-3}	4.815×10^{-2}
SO_4^{-2}	45.8	31.4	43.8	41.7	43.1	59.8
$NaSO_4^-$	18.3	1.6	9.7	9.8	2.8	19.4
$CaSO_4$	7.8	10.4	12.6	0.8	23.6	5.1
$FeSO_4$			-		-	-
$Al(SO_4)^{2-}$			-		-	-
$MgSO_4$	27.6	56.5	33.5	44.3	30.1	15.2
Si	1.978×10^{-4}	4.747×10^{-4}	1.1759×10^{-4}	2.164×10^{-4}	2.210×10^{-4}	4.537×10^{-4}
H_4SiO_4	99.7	98.2	98.9	98.2	99.0	99.6
Sr	1.870×10^{-4}	2.006×10^{-4}	4.737×10^{-4}	2.679×10^{-4}	1.428×10^{-4}	-
Sr^{+2}	88.0	91.6	87.0	59.7	96.3	-
$SrSO_4$	12.0	8.4	13.0	40.3	3.7	-

Table H3:(cont.) Speciation of paste extract samples

Elemental concentrations expressed in molality and speciation as a percentage.

Elements	S26	S27	S28	S29	S30
B	7.438×10^{-4}	3.430×10^{-4}	2.453×10^{-4}	5.644×10^{-4}	3.195×10^{-4}
H_3BO_3	98.6	99.6	95.6	100	97.8
$H_2BO_3^-$	1.4	0.4	4.4	-	2.2
Ca	1.729×10^{-2}	4.417×10^{-2}	2.070×10^{-2}	1.763×10^{-2}	1.738×10^{-2}
Ca^{+2}	75.0	93.4	90.4	86.4	72.8
$CaSO_4$	25.0	6.6	9.6	13.6	27.2
Cl	3.986×10^{-1}	4.609	8.141×10^{-1}	7.225×10^{-1}	5.580×10^{-1}
Cl^-	100	100	100	100	100
$FeCl^+$	-	-	-	-	-
Fe(2)	-	1.158×10^{-4}	-	-	-
Fe^{+2}	-	87.9	-	-	-
$FeCl^+$	-	11.5	-	-	-
$FeSO_4$	-	0.6	-	-	-
K	5.865×10^{-3}	6.151×10^{-2}	7.867×10^{-3}	6.580×10^{-3}	5.922×10^{-3}
K^+	95.7	99.9	98.6	97.9	95.1
KSO_4^-	4.3	0.1	1.4	2.1	4.9
Li	-	1.485×10^{-4}	-	-	-
Li^+	-	99.9	-	-	-
$LiSO_4^-$	-	-	-	-	-
Mg	4.143×10^{-2}	7.454×10^{-1}	1.745×10^{-1}	1.006×10^{-1}	6.064×10^{-2}
$MgSO_4$	30.9	14.0	13.2	18.2	34.1
Mg^{+2}	69.1	86.0	86.8	81.8	65.9
Mn (2)	-	-	-	-	3.349×10^{-4}
Mn^{+2}	-	-	-	-	57.9
$MnCl^+$	-	-	-	-	22.8
$MnSO_4$	-	-	-	-	16.9
Mn(3)	-	-	-	-	-
Mn^{+3}	-	-	-	-	-
N (5)	-	1.393×10^{-1}	3.389×10^{-2}	3.112×10^{-2}	-
NO_3^-	-	100	100	100	-
Na	4.227×10^{-1}	4.900	7.485×10^{-1}	6.588×10^{-1}	6.618×10^{-1}
Na^+	96.5	99.7	98.8	98.2	95.9
$NaSO_4^-$	3.5	0.3	1.2	1.8	4.1
S(6)	7.100×10^{-2}	1.450×10^{-1}	5.355×10^{-2}	5.802×10^{-2}	1.077×10^{-1}
SO_4^{-2}	54.8	16.9	36.0	43.7	50.9
$NaSO_4^-$	20.7	8.8	16.9	20.3	25.1
$CaSO_4$	6.1	2.0	3.7	4.2	4.4
$MgSO_4$	18.0	72.2	43.1	31.5	19.2
Si	3.399×10^{-4}	-	2.363×10^{-4}	4.968×10^{-4}	1.422×10^{-4}
H_4SiO_4	99.7	-	98.9	100	99.4
Sr	-	7.077×10^{-4}	1.618×10^{-4}	1.447×10^{-4}	-
Sr^{+2}	-	96.1	91.2	87.1	-
$SrSO_4$	-	3.9	8.8	12.9	-